## 467. π-Complexes of 8-Hydroxyquinoline and its Metal Complexes

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π-Complexes of 8-hydroxyquinoline and its copper, palladium, and nickel chelates with various electron acceptors have been prepared. Reflection spectra show new bands due to intermolecular charge transfer. These bands are shown to obey theoretical relationships known to be valid for organic π-donors. Ionisation potential and Hückel orbital energy values are deduced for the donor molecules from further relationships predicted on the same theory. These are discussed in terms of the interaction of metal $t_{2g}$ orbitals with ligand π orbitals, and correlated with intramolecular charge transfer bands of the chelates. The spectra of some organic complexes of new acceptors are discussed. The appearance of multiple charge transfer bands in tetracyanobenzene complexes is shown to be due to transitions from the highest filled donor orbital to the first two vacant orbitals of the acceptor.

CHARGE-transfer complexes of a wide variety of organic electron donor and acceptor molecules have been described, and reviewed recently by Briegleb.[1] We now report the preparation and charge-transfer spectra of a related type of complex, in which a purely organic electron donor is replaced by a metal complex with an aromatic ligand. The ligand, 8-hydroxyquinoline, forms stable, planar [2] complexes, soluble in organic solvents,[3] with many metal ions. This facilitates the preparation of stable π complexes. The electron acceptors used include several for which no spectral data have yet been published: benzotrifuroxan (I), benzotrifurazan (II), 4,6-dinitrobenzofuroxan, picryl azide, and 1,2,4,5-tetracyanobenzene (recently studied in solution complexes [4]). Relevant spectra are therefore reported for a variety of solid organic complexes of these acceptors.



*Results.*—Complexes of organic and metal chelate donors with ten electron acceptors were prepared and analysed (see Experimental section). Analytical figures for the complexes show that the donor : acceptor ratio is not always 1 : 1. In the complexes of

[1] G. Briegleb, " Elektronen Donator-Acceptor Komplexe," Springer–Verlag, Berlin, 1961.
[2] G. J. Palenik, *Acta Cryst.*, 1964, **17**, 687.
[3] R. G. W. Hollingshead, " Oxine and its Derivatives," Butterworth, London, 1954.
[4] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, 1963, **59**, 2287; A. Zweig, J. E. Lehnsen, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, 1963, **85**, 3937.

8-hydroxyquinoline and its metal chelates, the ratio is one acceptor molecule per 8-hydroxyquinoline nucleus, unless the acceptor is large (*e.g.*, trinitrofluorenone) or contains groups capable of specific interaction with the metal ion (*e.g.*, chloranil). Crystal-structure determinations for three of the complexes suggest that the lattice packing is a compromise between the tendency to maximise charge transfer and other attractive forces and the tendency to minimise repulsive forces due to the size and shape of the molecules, and this may also control the donor : acceptor ratio in the complexes.[5]

The spectra show new absorption bands in regions where neither of the component molecules absorb. Such bands are assigned to charge transfer, and are shown in Tables 1 and 2. In some cases, two or more distinct charge-transfer bands occur, and all are then recorded in the Tables.

TABLE 1

Charge-transfer band energies (kK) of 8-hydroxyquinolinato-complexes

| Reference number of acceptor for graphs | Acceptor *\ Donor | $Cu^{II}$ | $Pd^{II}$ | $Ni^{II}$ | 8-Hydroxy quinoline |
|---|---|---|---|---|---|
| 1 | BTF | 21·5 | 19·7 | 19·0[b] | — |
| 2 | TFZ | 22·7 | — | — | 26·0 |
| 3 | DNBF | 15·7 | 15·4 | — | — |
| 4 | TNB | 20·7 | — | — | 25·0 |
| 5 | Picryl azide | 19·6 | — | — | 24·4 |
| 6 | TNF | 18·2 | 17·0 | — | 21·9 |
| 7 | TCNB | 17·9 | 17·6 | — | 23·5 |
| 8 | Chloranil | 15·9 | 14·8 | 14·0[a] | 19·6[b] |
| 9 | DDQ | 12·9 | 12·1 | — | — |
| 10 | TCNE | 13·3[b] | 12·1[b] | 10·1[b] | — |

[a] Solution spectrum.  [b] Spectrum of impure solid complex.

* BTF, Benzotrifuroxan; TFZ, benzotrifurazan; DNBF, Dinitrobenzofuroxan; TNB, trinitro-benzene; TNF, trinitrofluorenone; DDQ, Dichlorodicyanobenzoquinone; TCNE, tetracyano-ethylene.

TABLE 2

Charge transfer band energies (kK)

| Reference number of donor for graphs | Donor \ Acceptor | BTF | TFZ | TCNB | Picryl azide | DNBF |
|---|---|---|---|---|---|---|
| 1 | Naphthalene | 27·4 | — | 24·5 | — | 22·2 |
| 2 | Anthracene | 21·5 | — | 19·7 25·5 | — | 16·0 |
| 3 | Pyrene | 22·9 | 23·3 | 19·8 25·4 | 21·3 | 16·7 |
| 4 | Phenanthrene | — | 27·0 | 23·4 | — | — |
| 5 | Chrysene | 23·8 | 25·0 | 21·7 | — | — |
| 6 | Perylene | — | 19·2 | — | — | — |
| 7 | Durene | — | 27·4 | 24·4 | — | — |
| 8 | Diphenyl | 26·9 | — | 25·8 | — | — |
| 9 | Azulene | 21·7 | 21·6 | 19·3 | — | — |
| 10 | β-Naphthol | 24·1 | — | 22·0 | — | 17·9 |
| 11 | Hexamethylbenzene | 26·3 | 26·2 | — | — | — |
| 12 | 1,4-Diphenylbutadiene | — | 24·1 | 21·5 | — | — |
| 13 | 1,5-Diaminonaphthalene | — | — | 15·9 22·8 28·8 | — | — |
| 14 | Dimethylaniline | — | — | 17·9 24·5 29·0 | — | — |
| 15 | Aniline | — | — | 21·0 29·2 | — | — |
| 20 | 2,7-Dimethoxynaphthalene | — | — | 23·4 29·8 | — | — |

[5] C. K. Prout and co-workers, personal communication.

## DISCUSSION

*Corresponding Complexes of Different Acceptor Molecules.*—The Mulliken theory [6] of charge-transfer bonding predicts small perturbations of the highest filled donor orbital and lowest vacant acceptor orbital, caused by charge-transfer resonance interactions. If these interactions are small (as in a weak complex) and approximately constant for a series of complexes with a common donor or acceptor, the following approximate relationships between the charge-transfer band energy and the ionisation potential of the donor or electron affinity of the acceptor can be deduced: [6b]

$$h\nu_{\text{C.T.}} \simeq k_1 I_{\text{D}}^{\text{v}} + k_2 \tag{1}$$

$$h\nu_{\text{C.T.}} \simeq k_1' - k_2' E_{\text{A}}^{\text{v}} \tag{2}$$

where $I_{\text{D}}^{\text{v}}$ = vertical ionisation potential of the donor, $E_{\text{A}}^{\text{v}}$ = vertical electron affinity of the acceptor, and $k_1$, $k_2$, $k_1'$, and $k_2'$ are constants.
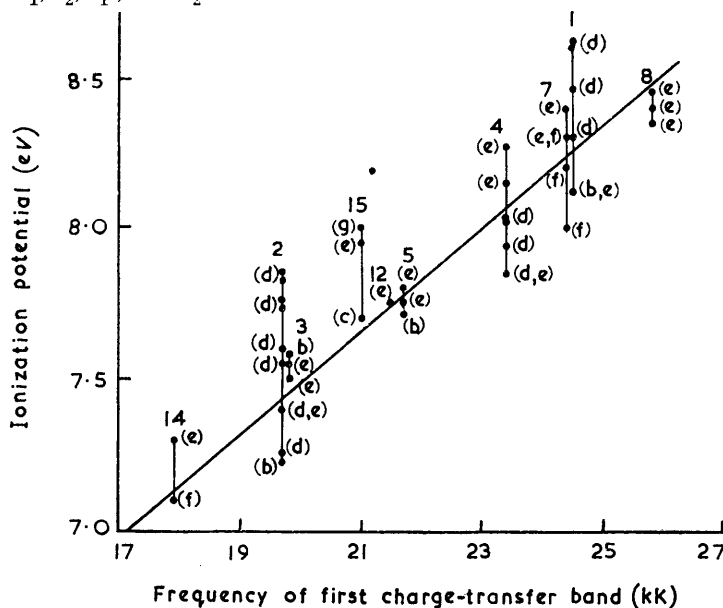


FIGURE I. The relationship between the ionisation potentials of donors and the frequency of the first charge transfer band. (The different points give different experimental values, the letters by each point representing the source of the ionisation potential, as in ref. 11.)

These equations form the basis of a comparative method for deducing ionisation potentials or electron affinities if there is evidence that the approximations involved are valid for the systems concerned. Such evidence can be obtained by plotting eqn. (1), provided ionisation potentials obtained by independent methods are available. This is done in Figure 1 for complexes of tetracyanobenzene with organic donors. A correlation exists, but the spread of experimental values for ionisation potentials prevents the use of this method for detecting small perturbation effects.

An alternative approach compares the predictions of a model involving no perturbations with actual spectral results. For a series of complexes with two acceptors, an energy-level diagram using unperturbed orbital energies for donor and acceptor molecules is shown in Figure 2. This diagram predicts that a plot of transition 1 against transition 2 should be linear, with unit slope and intercept equal to $\delta$, the difference in energies of the lowest vacant orbitals of acceptors 1 and 2. $\delta$ can also be obtained approximately by halving the energy difference of the first singlet transitions of the acceptors. These

[6] (a) R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; (b) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, 1962, **13**, 107.

occur at 315·6 and 258 mμ for TCNB and benzotrifuroxan (BTF) respectively so that δ equals 3500 cm.$^{-1}$. Figure 3 shows transition 2 plotted against transition 1 for these two acceptors. The least-squares line has slope 0·97 and intercept of 2700 cm.$^{-1}$ on the BTF axis. Thus there is satisfactory agreement with theory neglecting perturbation effects. The other new acceptors used have similar energy levels and shape, so the same arguments may be applied here.

By use of eqn. (2) and the method of Jortner and Sokolov,[7] the following electron affinities have been deduced from the spectral data (all values in electron volts): benzotrifuroxan, 1·9(8) ± 0·03 (mean of 6 values); benzotrifurazan, 1·9(2) ± 0·10 (mean of



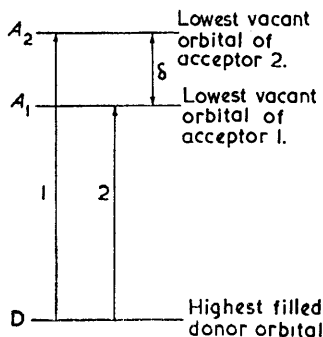FIGURE 2. Energy levels of donor, D, and acceptor, A

FIGURE 3. Relationship between the first charge transfer bands of BTF and TCNB complexes. Data in Tables
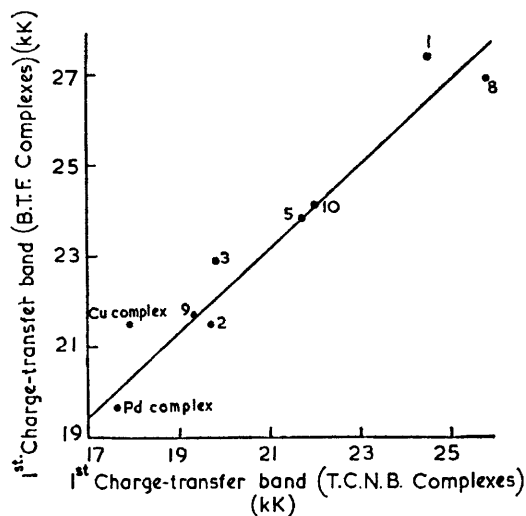


5 values); 1,2,4,5-tetracyanobenzene, 2·3(0) ± 0·06 (mean of 7 values); dinitrobenzofuroxan, 2·6(4) ± 0·09 (mean of 3 values).

Values for some of the other acceptors used are, for comparison: [7] tetracyanoethylene, 2·8(9) ± 0·10; chloranil, 2·5(9) ± 0·17; 1,3,5-trinitrobenzene, 1·8(6) ± 0·13.

The series of increasing acceptor strength trinitrobenzene < benzotrifuroxan ≏ benzotrifurazan < dinitrobenzofuroxan suggests that steric effects pushing nitro-groups out of plane in trinitrobenzene [8] have a considerable effect on its acceptor power.

The molecular orbital theory equivalent of eqn. (1) [9] is

$$hν_{C.T.} ≏ a + bχ.$$

[7] (a) J. Jortner and U. Sokolov, *Nature*, 1961, **190**, 1003; (b) M. Batley and L. E. Lyons, *ibid.*, 1962, **196**, 573.

[8] D. S. Brown, S. C. Wallwork, and A. Wilson, *Acta Cryst.*, 1964, **17**, 168.

[Here, $a = A_j - \alpha$ (where $A_j$ is the energy of the relevant ($j$th) vacant acceptor orbital, and $\alpha$ is the Coulomb integral for carbon) and $b = \beta$, the carbon–carbon resonance integral. $\chi$ is related to the energy of the donor orbital concerned by the equation $E = \alpha + \chi\beta$.] This equation has also been plotted for the TCNB complexes with organic donors. This gives a value for $\beta$ of $-3\cdot03$ ev, and, the Hückel type of expression being still assumed valid for TCNB, the energy of the lowest vacant orbital of the acceptor is given by

$$E = \alpha - 0\cdot37\beta$$

(where $\alpha =$ Coulomb integral for carbon, $\beta =$ carbon-carbon resonance integral). This compares with the values of $E = \alpha - 0\cdot46\beta$ for trinitrobenzene and $E = \alpha - 0\cdot11\beta$ for tetracyanoethylene obtained by Dewar and his co-workers.[9]

*Spectra of π-Complexes of 8-Hydroxyquinoline and its Metal Complexes.*—Figure 3 includes points for the bis-8-hydroxyquinolinato-copper(II) and -palladium(II) complexes, which are seen to fit reasonably on the line drawn for the hydrocarbon complexes. The
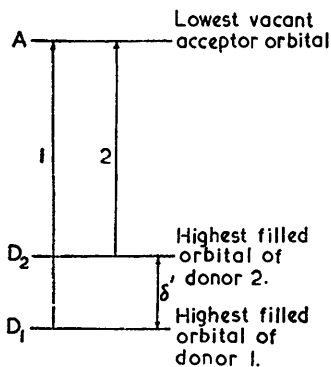


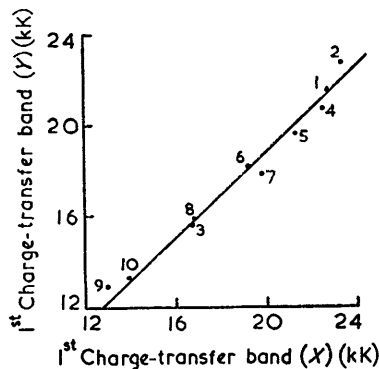FIGURE 4. Energy levels of two donors relative to one acceptor



FIGURE 5. Relationship between the first charge transfer bands of pyrene ($X$) and bis-8-hydroxyquinolinatocopper(II) ($Y$) complexes with a series of acceptors. Data in Tables

relationships between charge-transfer band energies, ionisation potentials and calculated orbital energies may therefore be extended to the complexes. Values for the vertical ionisation potentials and calculated orbital energies (Hückel $\chi$ values) for 8-hydroxy-quinoline and its copper and palladium complexes, deduced from these relationships are given in Table 3.

TABLE 3

|  | Ionisation potential (ev) | Hückel $\chi$ value |
|---|---|---|
| 8-Hydroxyquinoline ......... | $7\cdot9(4) \pm 0\cdot10$ (mean of 3 values) | $0\cdot5(7) \pm 0\cdot01$ (mean of 5 values) |
| Copper complex ............ | $7\cdot3(3) \pm 0\cdot07$ (mean of 4 values) | $0\cdot4(2) \pm 0\cdot03$ (mean of 6 values) |
| Palladium complex ......... | $7\cdot1(3) \pm 0\cdot11$ (mean of 3 values) | $0\cdot3(7) \pm 0\cdot02$ (mean of 4 values) |

Hückel LCAO molecular orbital theory calculations have recently been carried out for 8-hydroxyquinoline.[10] The calculated value of $\chi$ for the highest filled orbital of 8-hydroxy-quinoline in the neutral form is $+0\cdot552$, which agrees well with our observed value.

The spectra of 8-hydroxyquinoline complexes may also be compared with those of corresponding complexes of a hydrocarbon donor. Figure 4 shows an energy-level diagram analogous to Figure 2, predicting a linear plot of unit slope if transition 1 is plotted against transition 2. Figure 5 is such a plot for complexes with the copper chelate

[9] (a) M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, 1961, **83**, 4560; (b) M. J. S. Dewar and H. Rogers, *ibid.*, 1962, **84**, 395.

[10] R. E. Burton and W. J. Davis, *J.*, 1964, 1766.

and pyrene as donors. The least-squares slope is 0·94 and the intercept is 0·09 ev on the copper chelate axis. The experimental ionisation potentials [11] for pyrene, used with this intercept, give 7·6(3) ev as the ionisation potential for bis-8-hydroxyquinolinatocopper(II), although this method is probably less accurate than that used above.

The spectra shown in Figure 5 show no significant irregularities between 1 : 1 and 2 : 1 complexes of different structure. Deviations may, however, occur in properties depending on charge transfer throughout the lattice, as opposed to charge transfer between two molecules within a lattice, and we are at present studying photoconductivity in single crystals of these materials to investigate this possibility.

These results show that the energy levels of the highest filled orbitals for the 8-hydroxy-quinoline metal chelates are much higher than in the metal-free 8-hydroxyquinoline.
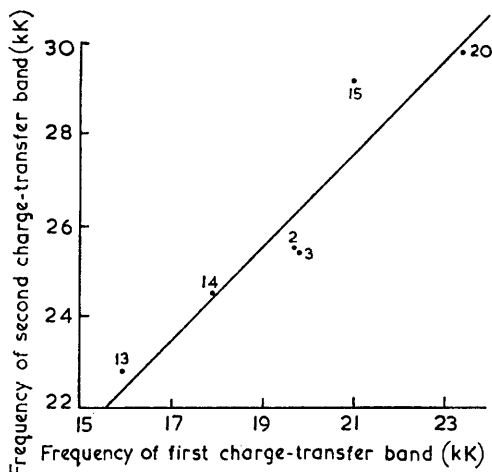


FIGURE 6. Relationship between the first and second charge transfer bands for tetracyanobenzene complexes. Data from Table 1

This suggests an extension of the delocalised π systems of the two 8-hydroxyquinoline groups through the central metal ions. The degree to which the $t_{2g}$ orbitals of the metal are exposed to the ligand π orbitals will control (i) the ease with which this extension of delocalisation occurs (as shown by the energy of the intermolecular charge transfer band in the π complex), and (ii) the ease with which transitions corresponding to intramolecular ligand–metal charge-transfer processes occur (as shown by characteristic chelate charge transfer bands). Thus, intramolecular charge-transfer bands for the Cu, Pd, and Ni chelates occur at 24,300, 23,100 and 22,000 cm.$^{-1}$, respectively,[12] which is the order of increasing π donor power as observed from the intermolecular charge transfer bands of the π complexes.

*The Appearance of Several Charge Transfer Bands in Tetracyanobenzene Complexes.—* Multiple charge-transfer bands may result from (i) transitions from several filled donor orbitals to a single vacant acceptor orbital, or (ii) transitions from the highest filled donor orbital to several vacant acceptor orbitals. In some cases (*e.g.,* tetracyanoethylene [13]) there is no low-lying second vacant acceptor orbital. In these cases, multiple charge-transfer bands are assigned to transitions of type (i). If there is a second low-lying vacant orbital with the correct symmetry for allowed transitions from the donor, both possibilities are available and overlap factors may decide which is actually favoured. More overlap is involved in higher transitions of type (ii) than in type (i). Thus, in tetracyanobenzene complexes, multiple charge-transfer bands are probably of type (ii).

[11] (a) F. H. Field and J. L. Franklin, *J. Chem. Phys.,* 1954, **22,** 1895; (b) F. A. Matsen, *ibid.,* 1956, **24,** 602; (c) K. Watanabe, *ibid.,* 1957, **26,** 542; (d) M. E. Wacks and V. H. Dibeler, *ibid.,* 1959, **31,** 1558; (e) G. Briegleb and J. Czekalla, *Z. Elektrochem.,* 1959, **63,** 9; (f) R. Foster, *Nature,* 1959, **183,** 1253; (g) H. Hartmann and M. B. Svendsen, *Z. Phys. Chem.,* 1957, NF **11,** 16.
[12] K. Sone, *J. Amer. Chem. Soc.,* 1953, **75,** 5208.
[13] A. Zweig, *Tetrahedron Letters,* 1963, 89.

A simplified energy-level scheme for these transitions is shown in Figure 2, where now $A_1$ and $A_2$ represent the first two vacant acceptor orbitals. A plot of the energy of the first charge-transfer band against that of the second band in the complexes should therefore be linear, with unit slope and intercept equal to the energy difference between the first two singlet transitions in tetracyanobenzene. Figure 6 shows this plot for complexes with organic donors. The least-squares line has slope 1·0 and intercept of 6600 cm.$^{-1}$. The first two singlet transitions of tetracyanobenzene are at 31,700 and 37,600 cm.$^{-1}$, corresponding to an energy gap of 5900 cm.$^{-1}$ between the first two vacant orbitals of tetracyanobenzene. These results confirm that the transitions are of type (ii).

## EXPERIMENTAL

*Materials.*—Benzotrifuroxan, benzotrifurazan, dinitrobenzofuroxan, picryl azide, and 1,2,4,5-tetracyanobenzene were prepared as described by Bailey *et al.*[14] Laboratory reagent grade 1,3,5-trinitrobenzene, 2,4,7-trinitrofluorenone, chloranil, and 2,3-dichloro-5,6-dicyanobenzoquinone were purified by recrystallisation. Tetracyanoethylene was as supplied by Kodak Ltd. All solvents were dried and redistilled. AnalaR 8-hydroxyquinoline was used to prepare copper(II), palladium(II), and nickel(II) chelates, as follows:

*Copper.* 8-Hydroxyquinoline (3 g.) in warm alcohol (30 ml.) was added to a solution of AnalaR copper acetate (2 g.) in hot water (150 ml.) with stirring. The solid was collected, washed well with hot water, and dried for several hours at 140°.

*Palladium.* Pd(NH$_3$)$_2$Cl$_2$ (0·21 g.) was dissolved in hot water and filtered into a solution of 8-hydroxyquinoline in glacial acetic acid. The yellow solid was washed well with hot water and dried for several hours at 120°.

*Nickel.* 8-Hydroxyquinoline (3 g.) in warm alcohol (30 ml.) was added to an acidic aqueous solution of AnalaR NiCl$_2$,6H$_2$O (2·4 g.), with stirring. The solid was washed well with hot water and dried for several hours at 140°.

*Preparation of the Complexes.*—The hydrocarbon complexes of benzotrifuroxan, benzotrifurazan, dinitrobenzofuroxan, picryl azide, and 1,2,4,5-tetracyanobenzene were prepared as described by Bailey and his co-workers.[14] Details of eight new *complexes* of the tetracyanobenzene are as follows (100 mg. of tetracyanobenzene used in each case).

*Naphthalene.* Made from naphthalene (75 mg.) in glacial acetic acid (8 ml.), this formed pale yellow rods, m. p. 257—263° (decomp.) (Found: C, 78·4; H, 3·4; N, 18·1. C$_{20}$H$_{10}$N$_4$ requires C, 78·4; H, 3·3; N, 18·3%).

*Phenanthrene.* Phenanthrene (100 mg.) in 2-methoxyethanol (3 ml.) gave yellow rods, m. p. 248—251° (decomp.) (Found: C, 80·5; H, 3·5; N, 16·2. C$_{24}$H$_{12}$N$_4$ requires C, 80·9; H, 3·4; N, 15·7%).

*Chrysene.* Chrysene (130 mg.) in 2-methoxyethanol (12 ml.) gave orange needles, m. p. 292—295° (decomp.) (Found: C, 82·4; H, 3·6; N, 13·7. C$_{28}$H$_{14}$N$_4$ requires C, 82·8; H, 3·4; N, 13·8%).

*Diphenyl.* Diphenyl (150 mg.; 1·5 molar excess) in 2-methoxyethanol (3 ml.) gave pale yellow rods, m. p. 211—214° (decomp.) (Found: C, 79·0; H, 3·8; N, 17·2. C$_{22}$H$_{12}$N$_4$ requires C, 79·5; H, 3·6; N, 16·9%).

*Azulene.* This (75 mg.) in glacial acetic acid (8 ml.) gave dark needles which decomposed without melting (Found: C, 78·0; H, 3·3; N, 18·8. C$_{20}$H$_{10}$N$_4$ requires C, 78·4; H, 3·3; N, 18·3%).

*Aniline.* Aniline (2 drops) in 2-methoxyethanol (3 ml.) produced dark red needles, m. p. 224—227° (decomp.) (Found: C, 70·5; H, 3·4; N, 25·8. C$_{16}$H$_9$N$_5$ requires C, 70·8; H, 3·4; N, 25·8%).

*Acenaphthylene.* Acenaphthylene (86 mg.) in glacial acetic acid (8 ml.) gave yellow rods, m. p. 298—302° (decomp.) (Found: C, 79·4; H, 3·4; N, 17·1. C$_{22}$H$_{10}$N$_4$ requires C, 80·0; H, 3·1; N, 16·9%).

*1,4-Diphenylbutadiene.* The butadiene (56 mg.) in 2-methoxyethanol gave bright red plates, m. p. 237—239° (decomp.) (Found: C, 76·4; H, 3·3; N, 20·1. C$_{16}$H$_{14}$,2C$_{10}$H$_2$N$_4$ requires C, 76·8; H, 3·2; N, 20·0%).

[14] A. S. Bailey and J. R. Case, *Tetrahedron*, 1958, **3**, 113; A. S. Bailey, *J.*, 1960, 917; A. S. Bailey, B. R. Henn, and J. Langdon, *Tetrahedron*, 1963, **19**, 161; A. S. Bailey and J. M. Evans, *Chem. and Ind.*, 1964, 1425.

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π-Complexes of 8-hydroxyquinoline and its metal complexes were prepared by dissolving the donor compound in a slight excess of the hot solvent, usually chloroform, and adding the calculated quantity of the solid acceptor. The solution was then warmed and filtered, and the complex allowed to crystallise slowly. Picryl azide complexes were prepared at below 40°c, to avoid decomposition. The *complexes* were washed with cold solvent and dried in a desiccator.

*Bis-8-hydroxyquinolinatocopper*(II) *Complexes.*—*With benzotrifuroxan.* Brown prisms from CHCl$_3$ [Found: C, 47·4; H, 2·1; N, 19·2; Cu, 10·3. Cu(C$_9$H$_6$NO)$_2$,C$_6$N$_6$O$_6$ requires C, 47·7; H, 2·0; N, 18·6; Cu, 10·5%].*

*With benzotrifurazan.* Fine mustard-coloured needles from C$_2$H$_2$Cl$_4$ [Found: C, 47·7; H, 1·9; N, 25·8; Cu, 8·3. Cu(C$_9$H$_6$NO)$_2$,2C$_6$N$_6$O$_3$ requires C, 47·5; H, 1·6; N, 25·8; Cu, 8·3%].

*With dinitrobenzofuroxan.* Brown microcrystals from CHCl$_3$ [Found: C, 50·0; H, 3·2; N, 14·7; Cu, 10·4. Cu(C$_9$H$_6$NO)$_2$,C$_6$H$_2$N$_4$O$_6$ requires C, 49·9; H, 2·4; N, 14·5; Cu, 11·0%].

*With trinitrobenzene.* Dark red needles from C$_2$H$_2$Cl$_4$ [Found: C, 46·3; H, 2·7; N, 14·3; Cu, 8·1. Cu(C$_9$H$_6$NO)$_2$,2C$_6$H$_3$N$_3$O$_6$ requires C, 46·3; H, 2·3; N, 14·4; Cu, 8·2%].

*With picryl azide.* Dark red needles from C$_2$H$_2$Cl$_4$ [Found: C, 41·7; H, 2·1; N, 23·0; Cu, 7·3. Cu(C$_9$H$_6$NO)$_2$,2C$_6$H$_2$N$_6$O$_6$ requires C, 41·9; H, 1·9; N, 22·8; Cu, 7·4%].*

*With trinitrofluorenone.* Brown microcrystals from CHCl$_3$ and C$_2$H$_2$Cl$_4$ [Found: C, 56·2; H, 3·0; N, 10·3; Cu, 9·2. Cu(C$_9$H$_6$NO)$_2$,C$_{13}$H$_5$N$_3$O$_7$ requires C, 55·8; H, 2·6; N, 10·5; Cu, 9·5%].

*With tetracyanobenzene.* Black needles from CHCl$_3$ [Found: C, 64·0; H, 1·8; N, 20·4; Cu, 8·9. Cu(C$_9$H$_6$NO)$_2$,2C$_{10}$H$_2$N$_4$ requires C, 64·5; H, 2·5; N, 19·8; Cu, 9·0%].

*With chloranil.* Blue-violet needles from CHCl$_3$ [Found: C, 48·5; H, 2·4; Cl, 23·8; N, 5·1; Cu, 10·5. Cu(C$_9$H$_6$NO)$_2$,C$_6$O$_2$Cl$_4$ requires C, 48·2; H, 2·0; Cl, 23·7; N, 4·7; Cu, 10·6%].

*With dichlorodicyanoquinone.* Dark green microcrystals from CHCl$_3$ [Found: C, 53·9; H, 2·1; Cl, 12·0; N, 9·0; Cu, 11·0. Cu(C$_9$H$_6$NO)$_2$,C$_8$Cl$_2$N$_2$O$_2$ requires C, 53·9; H, 2·1; Cl, 12·2; N, 9·7; Cu, 11·0%].

*Bis-8-hydroxyquinolinatopalladium*(II) *Complexes.*—*With benzotrifuroxan.* Scarlet needles from CHCl$_3$ [Found: C, 44·5; H, 1·9; N, 17·5; Pd, 16·4. Pd(C$_9$H$_6$NO)$_2$,C$_6$N$_6$O$_6$ requires C, 44·5; H, 1·9; N, 17·3; Pd, 16·5%].*

*With dinitrobenzofuroxan.* Brown microcrystals from CHCl$_3$ [Found: C, 45·0; H, 3·1; N, 13·3; Pd, 16·0. Pd(C$_9$H$_6$NO)$_2$,C$_6$H$_2$N$_4$O$_6$ requires C, 46·4; H, 2·3; N, 13·5; Pd, 17·1%].

*With trinitrofluorenone.* Brown microcrystals from CHCl$_3$ [Found: C, 52·0; H, 2·3; N, 9·8; Pd, 15·0. Pd(C$_9$H$_6$NO)$_2$,C$_{13}$H$_5$N$_3$O$_7$ requires C, 52·4; H, 2·4; N, 9·9; Pd, 15·0%].

*With tetracyanobenzene.* Very dark red prisms from CHCl$_3$ [Found: C, 58·5; H, 2·5; N, 14·8; Pd, 18·1. Pd(C$_9$H$_6$NO)$_2$,C$_{10}$H$_2$N$_4$ requires C, 58·7; H, 2·5; N, 14·8; Pd, 18·6%].*

*With chloranil.* Very dark green needles from CHCl$_3$ [Found: C, 46·0; H, 2·0; Cl, 22·3; N, 4·5; Pd, 16·5. Pd(C$_9$H$_6$NO)$_2$,C$_6$O$_2$Cl$_4$ requires C, 45·0; H, 1·9; Cl, 22·1; N, 4·4; Pd, 16·6%].*

*With dichlorodicyanoquinone.* Dark blue-green powder from CHCl$_3$ [Found: C, 50·2; H, 2·2; Cl, 11·8; N, 7·6; Pd, 16·9. Pd(C$_9$H$_6$NO)$_2$,C$_8$N$_2$O$_2$Cl$_2$ requires C, 50·2; H, 1·9; Cl, 11·4; N, 9·0; Pd, 17·1%].

*8-Hydroxyquinoline Complexes.*—*With benzotrifuroxan.* Pale yellow plates from n-propanol [Found: C, 52·9; H, 2·6; N, 21·0. (C$_9$H$_7$NO)$_2$,C$_6$N$_6$O$_6$ requires C, 52·1; H, 2·6; N, 20·7%].

*With benzotrifurazan.* Yellow needles from methanol (Found: C, 50·6; H, 2·1; N, 28·6. C$_9$H$_7$NO,C$_6$N$_6$O$_3$ requires C, 51·6; H, 2·0; N, 28·2%).

*With trinitrobenzene.* Yellow needles from glacial acetic acid (Found: C, 50·5; H, 2·7; N, 16·0. C$_9$H$_7$NO,C$_6$H$_3$N$_3$O$_6$ requires C, 50·3; H, 2·8; N, 15·6%).

*With picryl azide.* Yellow needles from ethanol (Found: C, 45·5; H, 2·3; N, 24·7. C$_9$H$_7$NO,C$_6$H$_2$N$_6$O$_6$ requires C, 45·1; H, 2·3; N, 24·6%).

*With trinitrofluorenone.* Fine orange needles from ethanol [Found: C, 61·6; H, 3·2; N, 11·6. (C$_9$H$_7$NO)$_2$,C$_{13}$H$_5$N$_3$O$_7$ requires C, 61·5; H, 3·2; N, 11·6%].

*With tetracyanobenzene.* Yellow needles from glacial acetic acid (Found: C, 70·0; H, 2·8; N, 21·9. C$_9$H$_7$NO,C$_{10}$H$_2$N$_4$ requires C, 70·6; H, 2·8; N, 21·7%).

*Bis-8-hydroxyquinolinatonickel*(II) *Complexes.*—These have not been isolated as pure solids, owing to the very poor solubility of bis-8-hydroxyquinolinatonickel(II) in suitable solvents. However, impure complexes (containing some of the free nickel complex) have been isolated for benzotrifuroxan, tetracyanoethylene, and chloranil, and the charge-transfer bands of these

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* *X*-Ray crystallographic measurements support analytical figures for stoicheiometries in these compounds.

solids agree with the new bands in solution spectra of the mixed components. Addition of dichlorodicyanobenzoquinone to solutions of 8-hydroxyquinoline or its nickel complex in chloroform gives a transient charge transfer colour, which fades rapidly, with formation of a yellow precipitate. These reactions are due to a secondary reaction, following, and probably assistd by, formation of the charge-transfer complex in solution.

*Spectra.*—Diffuse reflection spectra were obtained from the Unicam S.P. 500 spectrophotometer with reflection attachment. Milligram samples of the complexes were ground with one gram of AnalaR potassium bromide for 1 hr. in a mechanical agate mortar, and compared with a reference of potassium bromide ground alone for an identical period. This technique reduces the effect of the regular reflectance,[15] and the dilution effect reduces the maximum optical density to be measured, thereby improving resolution considerably.

[15] G. Kortum, *Trans. Faraday Soc.*, 1962, **58**, 1624.