Transition-metal Complexes of the 2,3-Dipyridylquinoxalines. Part I. Cobalt(II), Nickel(II), and Copper(II) Halide Derivatives of 2,3-Di-(2-pyridyl)quinoxaline

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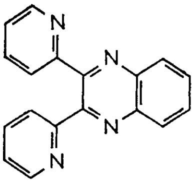
The cobalt(II), nickel(II), and copper(II) halide complexes of 2,3-di-(2-pyridyl)quinoxaline are described, and the structures interpreted on the basis of magnetic and spectral data. For cobalt, the tetrahedral complexes $CoX_2(DPYQ)$ where X = Cl and Br, and $CoX_2(DPYQ)_2$ where X = Br and I, were isolated. For copper both the chloro- and bromo-complexes have stoicheiometry $CuX_2(DPYQ)$, though with different structures. The nickel complexes follow a less well ordered pattern, though both the complexes isolated pure, $Ni_2Cl_4(DPYQ)(H_2O)_2$ and $NiBr_2(DPYQ)$, are believed to be octahedral.

EARLIER we reported [1] on the complexes formed by the chelated ene-diol 2,2′-pyridoin, and the diketo-analogue 1,2-di-(2-pyridyl)ethane-1,2-dione (2,2′-pyridil). As an extension of this work the ligand 2,3-di-(2-pyridyl)-quinoxaline (hereafter called DPYQ) has been prepared by condensation of the dione with *o*-phenylenediamine, and the complexes formed by this ligand have been investigated.

RESULTS AND DISCUSSION

General Structural Considerations.—The ligand DPYQ was prepared by Goodwin and Lions [2] as part of an investigation of pseudo-phenanthroline systems, the structure being written as (I). The copper chloride complex was prepared, and it was shown that with iron(II) DPYQ gave a transient red-purple colour in solution, and a paramagnetic solid complex $FeCl_2(DPYQ)$. It was therefore concluded that DPYQ is not strictly analogous to *o*-phenanthroline, and co-ordinates abnormally.



(I)

Molecular models show a number of points fundamental to the way in which DPYQ may act as a ligand.

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[1] M. Brierley and W. J. Geary, *J. Chem. Soc.* (*A*), 1967, 321.

[2] H. A. Goodwin and F. Lions, *J. Amer. Chem. Soc.*, 1959, **81**, 6415.

(i) Because of steric interactions between protons attached to the 6-position of the pyridine rings (the pyridine N atoms being assumed *cis* to the quinoxaline N atoms), or between the pyridine N atoms (if they are *trans* to the quinoxaline N atoms) it is not possible for the pyridine rings to be coplanar with the quinoxaline system. It is thus clear why DPYQ is not strictly analogous to *o*-phenanthroline.

(ii) It has been shown by Underhill and his co-workers [3-5] that the related ligand 2,3-diphenylquinoxaline (DPQ) does not form complexes with Co^{II} and Ni^{II} and functions as a unidentate non-bridging ligand in the complexes $CuX_2(DPQ)_2$. Since DPYQ readily forms complexes with Co^{II}, Ni^{II}, and Cu^{II}, having stoicheiometry and properties in most cases reconcilable only with its function as a bidentate ligand (and in some cases bis-bidentate), it seems that a formal analogy with the diphenyl ligand may be discounted. Thus a structure in which steric repulsions are minimised by the pyridine rings' being perpendicular to the quinoxaline system cannot apply, since this would place the pyridine and quinoxaline N atoms in positions relative to each other which could not lead to chelate formation. However, there is a possibility that in this configuration DPYQ could function as a bis-unidentate ligand, bridging MX_2 units, provided the M–X bonds are perpendicular to the quinoxaline system, and coplanar with the pyridine rings.

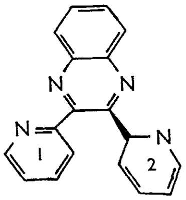
TABLE 1

Complexes formed by 2,3-di-(2-pyridyl)quinoxaline

Complex	Colour	μ_{eff} (B.M.)	Found (%)			Required (%)		
			M	N	X	M	N	X
$CoCl_2L$	Green	4·70	14·48	13·62	17·13	14·24	13·54	17·13
$CoBr_2L$	Green	4·70	11·72	11·21	31·55	11·81	11·14	31·77
$CoBr_2L_2$	Red-Brown	4·92	7·47	14·38	19·95	7·49	14·24	20·30
CoI_2L_2	Dark brown	4·89	6·73	12·33	28·53	6·69	12·72	28·80
$Ni_2Cl_4L(H_2O)_2$	Bright yellow *	3·46	20·37	9·45	24·70	20·26	9·67	24·48
$NiBr_2L$	Orange brown	3·18	11·49	10·84	31·67	11·68	11·15	31·79
$CuCl_2L$	Green *	1·98	15·14	13·09	16·90	15·18	13·39	16·93
$CuBr_2L$	Khaki *	1·95	12·61	11·17	31·34	12·52	11·04	31·49

* Precipitated immediately, or shortly after mixing.

(iii) By analogy with the crystal structure determined [6] for the parent dione 2,2'-pyridil, a possible structure for DPYQ is for one pyridine ring to be coplanar with the quinoxaline system, and the other to be approximately at right angles (II). DPYQ would then function as a bidentate non-bridging ligand. The only objection to this structure is that 2,3-di-(6-methyl-2-pyridyl)-quinoxaline functions similarly to DPYQ,[7] and for this ligand a methyl group in the 6-position of ring 1 interacts somewhat with ring 2.



(II)

(iv) The most probable structure is one in which the pyridine rings are effectively parallel, and at roughly 45° to the plane of the quinoxaline system. This places the pyridine N atoms slightly above and below the plane of the quinoxaline system respectively, but still in a position for chelate formation, and also allows the 6,6-dimethyl analogue to function similarly.

In conclusion, it seems that the mode of co-ordination adopted by DPYQ is dictated by the stereochemical requirements of the metal ion, the different configurations being adopted by rotation of the pyridine rings.

Cobalt(II) *Complexes*.—From the magnetic and spectral data (Tables 1 and 2) all the cobalt(II) complexes are clearly tetrahedral. The band assignments, and the calculated crystal field parameters, obtained from the reflectance spectra, are given in Table 3. For the complexes $CoBr_2(DPYQ)_2$ and $CoI_2(DPYQ)_2$ there is good agreement of the *Dq* values with those reported [4] for the

TABLE 2

Visible and near-i.r. spectra of complexes (kK)

(*a*) Reflectance spectra

$CoCl_2L$	24·6, 18·2sh, 16·2, 15·8sh, 15·4sh, 10·6, 8·9sh, 5·5
$CoBr_2L$	24·3, 20·75sh, 17·9sh, 16·0, 15·2sh, 14·7sh, 10·9, 8·9sh, 5·4
$CoBr_2L_2$	19·7, 18·7, 17·1, 16·2sh, 14·3sh, 9·5, 6·8
CoI_2L_2	21·7, 19·1, 16·4, 14·5, 13·3sh, 9·6, 6·8
$Ni_2Cl_4L{\cdot}2H_2O$	34·5, 25·8, 23·4sh, 12·9, 11·1sh, 8·7, 7·5sh
$NiBr_2L$	34·5, 24·5, 22·9sh, 20·0sh, 14·3sh, 11·4sh, 8·6, 7·5sh
$CuCl_2L$	29·0, 13·7vbr
$CuBr_2L$	28·6, 20·0sh, 13·3vbr

All complexes showed bands due to the ligand at 6·0, 4·6, 4·35, and 4·1 kK

(*b*) Solution spectra (ethanol) with molar extinctions in parentheses

$CoCl_2L$	17·4 (308), 15·9 (394), 15·4 (370), 14·7sh (253)
$CoBr_2L$	16·75 (349), 15·5 (513), 15·0 (521)
$CoBr_2L_2$	16·8 (370), 15·5 (508), 15·0 (508) *
CoI_2L_2	23·5sh (1931),† 15·85 (503), 14·95 (667), 14·2 (657) *

* Presumably spectrum of CoX_2L. † Shoulder on charge-transfer band.
sh = Shoulder, vbr = very broad

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[3] D. E. Billing, A. E. Underhill, and G. M. Smart, *J. Chem. Soc.* (*A*), 1968, 8.

[4] D. E. Billing and A. E. Underhill, *J. Chem. Soc.* (*A*), 1968, 5.

[5] D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris, *J. Chem. Soc.* (*A*), 1966, 902.

[6] S. Hirokawa and T. Ashida, *Acta Cryst.*, 1961, **14**, 775.

[7] W. J. Geary, to be published.

TABLE 3

Crystal field parameters for tetrahedral cobalt complexes

	ν_2	ν_3	*Dq*	*B*
$CoCl_2L$	5·51	16·2	0·315	0·82
$CoBr_2L$	5·39	16·0	0·31	0·81
$CoBr_2L_2$	6·76	17·1	0·39	0·81
CoI_2L_2	6·80	16·4	0·39	0·76

All values are in kK.

analogous quinoxaline complexes, suggesting a similar co-ordination arrangement involving a monomeric complex with two non-bridging unidentate DPYQ molecules. The complexes $CoCl_2$(DPYQ) and $CoBr_2$(DPYQ) have significantly lower values of *Dq* and higher values of *B*, and this may be explained in two ways. The complexes could be halogen-bridged dimers with the Co^{II} ion having an environment of three halogen and one nitrogen atoms, and unidentate DPYQ molecules, or they could be monomers with bidentate non-bridging ligand molecules. In the second case the steric hindrance would be minimised by a lengthening of the Co–N bonds and a consequent lowering of *Dq*.[8] The i.r. data are discussed later, but it is noteworthy that the bis-DPYQ complexes have spectra which are similar to the DPYQ complex of iodine monochloride,[7] I(DPYQ)Cl, in which the ligand, by virtue of the linear bonding requirements of the iodine atom, can only be unidentate. The mono-DPYQ complexes have spectra which are different from the bis-DPYQ complexes and from the ICl–DPYQ complex. This suggests that the ligand is co-ordinating in a different fashion in the mono- and bis-DPYQ complexes, and hence supports the monomeric formulation of CoX_2(DPYQ). In support of this, the solution spectrum of $CoBr_2(DPYQ)_2$ is identical with that of $CoBr_2$(DPYQ), and it seems probable that on dissociation of one molecule of ligand from the complex the vacant co-ordination site would be taken up by the remaining DPYQ molecule, rather than by dimerisation, particularly in the very dilute solutions used.

The spectrum of $CoI_2(DPYQ)_2$ in solution is quite different from the reflectance spectrum of the solid, and much more like that of $CoBr_2$(DPYQ), suggesting that dissociation to CoI_2(DPYQ) occurs in solution. The latter complex could not be obtained solid, and despite repeated efforts no evidence could be obtained for a complex $CoCl_2(DPYQ)_2$.

Thermal conversions of bis-quinoxaline into mono-quinoxaline complexes have been used previously,[4] and were found applicable in this case. $CoBr_2(DPYQ)_2$ started to lose weight slowly at 250°, and was held at 300° to constant weight (ambient temperatures). The weight loss of 35·3% compares favourably with loss of one ligand molecule (36·1%). In an identical experiment $CoI_2(DPYQ)_2$ lost 29·8% (theory for one DPYQ = 32·25%), the product being a black solid showing signs of decomposition.

Copper(II) *Complexes*.—By virtue of the stoicheiometry CuX_2(DPYQ) of these complexes the ligand must be functioning differently from diphenylquinoxaline $(DPQ)_2$ the complexes $CuX_2(DPQ)_2$ isolated previously.[5] In agreement with that work, molecular models show that DPYQ cannot bridge planar chains of $[CuX_4]^{2-}$ units. However, the visible spectrum of $CuCl_2$(DPYQ) is characteristic of six-co-ordinate copper (single broad band at 730 mμ), and requires the DPYQ ligands to be bridging and chelating. This would be expected to lead to a tetragonal environment commonly found for the Cu^{II} ion.

The spectrum of $CuBr_2$(DPYQ) is quite different from that of the chloride, particularly in having a strong and well defined shoulder at 500 mμ on the charge-transfer band. This effect has been noted previously[5,9,10] for several systems where steric hindrance occurs, and has been assigned to a square planar arrangement around the Cu^{II} ion. The i.r. spectrum of $CuBr_2$(DPYQ) lends no support for unidentate bridging DPYQ, and the structure must therefore contain bidentate non-bridging DPYQ and a *cis*-planar Cu^{II} environment. Both the complexes CuX_2(DPYQ) were insoluble in organic solvents, and solution spectra could not be obtained.

Nickel(II) *Complexes*.—Although DPYQ readily forms complexes with nickel(II) halides, the products obtained present greater problems of interpretation than those of cobalt(II) and copper(II). The nickel chloride complex, dried initially at 100° as for all the other complexes, has the formula Ni_2Cl_4(DPYQ),$2H_2O$. The material does not lose the water molecules until approximately 150°, and it is clear that these must be considered as co-ordinated to the Ni^{II} ion. The i.r. spectrum of the dried material also demonstrates the presence of the water molecules. The reflectance spectrum is characteristic of octahedral Ni^{II}, and the magnetic moment of 3·46 B.M. also indicates an octahedral structure, though moments at the top end of the octahedral range are usually taken to indicate strong tetragonal distortions.[11] Following previous assignments for tetragonally distorted Ni^{II} complexes,[12,13] the main band at 8·7 kK and the shoulder at 11·1 kK may be taken as the split components of ν_1 for $^3A_{2g} \rightarrow {}^3T_{2g}(F)$. The separation of the split components (2400 $cm.^{-1}$) is thus in the same range as that for NiL_4X_2 (L = heterocyclic amine).[12] The stoicheiometry of the system and the strong tetragonal distortion can best be satisfied on the basis of structure (III), in which a DPYQ molecule, functioning as a bis-bidentate ligand, bridges two nickel(II) ions, the remaining positions around each nickel being occupied by two bridging Cl^- (probably in the axial positions), a non-bridging Cl^-, and a water molecule (probably in the equatorial positions). Meaningful comparisons of the *Dq* value for this highly unsymmetrical array with other more regular systems cannot be made, though it may be noted that the value is rather higher than for other quinoxaline systems.[3,11]

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[8] A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.* (*A*), 1966, 859.

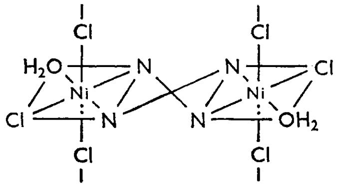
[9] M. Brierley and W. J. Geary, *J. Chem. Soc.* (*A*), 1967, 963.

[10] M. Brierley and W. J. Geary, *J. Chem. Soc.* (*A*), 1968, 1641.

[11] A. B. P. Lever, *J. Inorg. Nuclear Chem.*, 1965, **27**, 149.

[12] S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 1965, 3276.

The orange-brown complex $NiBr_2$(DPYQ) has a magnetic moment (3·18 B.M.) which suggests an octahedral environment for the nickel(II) ion. The reflectance spectrum consists of three main bands, at 34·5, 24·9, and 8·6 kK respectively, and a series of rather ill-defined shoulders between the second and third bands. These data, in conjunction with the stoicheiometry, indicate that the complex is essentially similar to the complex $CuCl_2$(DPYQ), having bis-bidentate DPYQ molecules bridging $NiBr_2$ units.



(III)

The nickel iodide complex of DPYQ could only be obtained (as a brown solid) by complete removal of the solvent used in the preparation, and the material so obtained was not completely pure. However, it was clear that the complex had stoicheiometry NiI_2(DPYQ), and the magnetic moment (*ca.* 3·25 B.M.) supports an analogous structure to the bromide.

TABLE 4

Infrared data for 2,3-di-(2-pyridyl)quinoxaline and its complexes (625—4000 cm.$^{-1}$; all bands medium or strong unless specified)

Ligand	1592, 1572, 1557, 1481, 1455sh, 1441, 1431, 1398, 1351, 1328, 1295w, 1282, 1262, 1240w,br, 1152, 1141, 1130, 1091, 1076, 1051w, 1043w, 1035w, 998, 985, 980sh, 962w, 957w, 898, 874w, 822, 809, 791, 763, 758, 748sh, 744, 730w, 720, 707.
All complexes	1600 ± 5, *1574 ± 2, 1563, *1482 ± 5, *1443 ± 5, 1361 ± 5, 1302 ± 2, *1260 ± 3, 1225 ± 5, *1153 ± 3, 1121 ± 5, 1082 ± 3, 1056 ± 4, *997 ± 3, *821 ± 4, *790 ± 3, 781 ± 4, *752 ± 2, 707 ± 2.
$CuCl_2L$	1403w, 1332w, 1292w, 1250, 1167sh, 1161, 1131, 1109, 1063sh, 1042w, 1028, 806w, 784sh, 773, 767, 758, 652.
$CuBr_2L$	1403w, 1332w, 1292w, 1247w, 1167sh, 1149w, 1131w, 1110, 1062sh, 1038w, 1028, 805, 782sh, 769, 765, 757, 652.
$CoCl_2L$	1590, 1326w, 1286w, 1248, 1241w, 1167w, 1156, 1134w, 1092, 1053, 1024w, 1015w, 990, 812, 772, 768, 748, 732w, 713w, 653.
$CoBr_2L$	1587, 1328w, 1285w, 1247w, 1239w, 1166, 1133, 1093, 1052, 1026w, 990, 908w, 810, 768, 745, 731w, 712w, 655.
$CoBr_2L_2$	1587, 1333sh, 1247, 1241, 1164sh, 1134, 1114, 1099, 1042w, 1015, 962w, 811w, 774, 762, 755, 749, 714w, 644.
CoI_2L_2	1585, 1333sh, 1287sh, 1247, 1239, 1163sh, 1133, 1098, 1044, 1031sh, 1018sh, 1015, 987w, 971w, 962w, 959w, 825, 811, 784, 770, 760, 746, 732w, 712, 644.
$Ni_2Cl_4L(H_2O)_2$	3300br, 1661, 1653sh, 1504w, 1290, 1235sh, 1110w, 1062, 1045sh, 1029, 964w, 767, 760, 655.
$NiBr_2L$	1496, 1287, 1267, 1235w, 1171, 1156sh, 1145sh, 1109, 1048, 1025, 1019sh, 990sh, 982w, 961, 920, 912w, 762, 757, 711, 652.

* Bands present in ligand.
w = Weak, sh = shoulder, br = broad.

Infrared Spectra.—Details of the spectra are in Table 4. All the spectra are very complex, the ligand itself having some 30 bands in the region of study, and correlations with the structures of the complexes are thus difficult to find. The complexes $CoX_2(DPYQ)_2$, in which the ligand must be unidentate and non-bridging, significantly have spectra identical in practically all respects with the complex I(DPYQ)Cl, in which DPYQ must also function in this way. These three complexes have bands at 1098 ± 1 cm.$^{-1}$ and 644 cm.$^{-1}$, which are absent from all other complexes, and it seems likely that these bands are associated with unidentate DPYQ. All other complexes have a band between 650—655 cm.$^{-1}$ which may be associated with bidentate DPYQ, but it is not possible to distinguish bands due to bridging and non-bridging ligand.

Significant new bands in the complexes occur at 1225 ± 5, 1056 ± 4, and 781 ± 4 cm.$^{-1}$, whilst shifts in some of the stronger ligand bands are 1592 $\longrightarrow$ 1600, 1557 $\longrightarrow$ 1563, 1351 $\longrightarrow$ 1361, 1282 $\longrightarrow$ 1302, 1091 $\longrightarrow$ 1121, and 1076 $\longrightarrow$ 1082 cm.$^{-1}$. The regions of most intense absorption, both for the ligand and complexes, are 1000—1170 and 741—825 cm.$^{-1}$. In the former region there are five strong ligand bands, two of which (1152, 1130 cm.$^{-1}$) recur for the complexes, whilst two are shifted as noted above. The fifth band, at 1141 cm.$^{-1}$, is not found for the complexes. In the second region there are seven strong ligand bands, though the complexes, with the exception of $CoBr_2$(DPYQ) and the two nickel complexes, have at least one additional band in this range.

EXPERIMENTAL

Magnetic, thermogravimetric, and visible spectral measurements were made as before.[9,10] I.r. spectra of mulls in Nujol were recorded on Grubb-Parsons Spectromaster and Unicam SP 200 instruments.

2,3-Di(2-pyridyl)quinoxaline was prepared by refluxing equimolar quantities of 2,2-pyridil and *o*-phenylenediamine in ethanol for 6 hr. Solvent was removed, and the precipitated solid recrystallised from ethanol using charcoal (Found: C, 76·31; H, 4·05; N, 19·66. Calc. for $C_{18}H_{12}N_4$; C, 76·03; H, 4·25; N, 19·72%). It had m.p. 183—184° (lit.,[2] 180°; lit.,[14] 185°).

The *complexes* were prepared by the general method of mixing the appropriate molar quantities of ligand and metal salt in ethanol (total volume *ca.* 200 ml.), and refluxing for approximately 2 hr. They were precipitated either on mixing the solution, or on removal of a quantity of solvent, and were purified either by thorough washing with, or recrystallisation from, ethanol, and were dried at 100° followed by storage in a desiccator. Details are in Table 1.

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[13] O. Bostrup and C. K. Jorgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

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