Transition-metal Complexes of the 2,3-Dipyridylquinoxalines. Part IV.[1] Cobalt(II), Nickel(II), and Copper(II) Halide Derivatives of 6-Methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline and 6,7-Dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline

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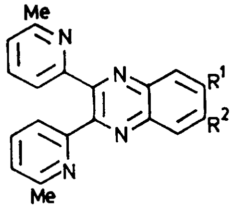
The cobalt(II), nickel(II), and copper(II) halide complexes of 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dpq) and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dmpq) are described, and the structures are interpreted on the basis of magnetic and spectral data. For cobalt and nickel, the complexes MX_2(dpq) (M = Co, Ni; X = Cl, Br, I) and MX_2(dmpq) (M = Co; X = Cl, Br, I; M = Ni; X = Br, I) were isolated and shown to be essentially tetrahedral. $NiCl_2$(dmpq), which has a distorted octahedral structure, was also isolated. The complexes $CuCl_2$(dpq) and Cu_2Cl_4(dmpq) have square planar structures, but the data for $CuBr_2$(dpq) do not allow conclusive structural assignments to be made. The solution properties of the complexes are described and interpreted.

We recently described the complexes formed by 6-methyl-2,3-di-(2-pyridyl)quinoxaline and 6,7-dimethyl-2,3-di-(2-pyridyl)quinoxaline with the halides of cobalt(II), nickel(II), and copper(II).[1] Here we report the complexes formed by the related ligands 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dpq) (I; R^1 = Me, R^2 = H), and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dmpq) (I; $R^1 = R^2$ = Me) with the same series of metal halides.



(I)

RESULTS AND DISCUSSION

The structural implications of the unsubstituted analogue 2,3-di-(2-pyridyl)quinoxaline were discussed previously [2] and again seem valid for the present ligands, the pyridyl rings probably being essentially parallel to each other and *ca.* 45° to the quinoxaline system. The possible modes of co-ordination of the ligand are then (i) unidentate non-bridging, (ii) bidentate non-bridging, (iii) bis-unidentate bridging, (iv) bis-bidentate bridging, and (v) unidentate bidentate bridging. However, the presence of bulky substituents adjacent to possible co-ordination sites can hinder the co-ordination of more than one ligand molecule,[3] and hence the presence of bridging ligand may not be expected.

The ligands dpq and dmpq readily form complexes with cobalt(II), nickel(II), and copper(II) halides in ethanolic solution, the complexes being precipitated on slow removal of solvent. Most of the complexes are soluble in organic solvents, and molecular-weight measurements show that the majority of them are monomeric.

Previously,[1,2,4] we have made use of the i.r. spectra of the complexes to distinguish between unidentate and bidentate ligand co-ordination, and similar considerations are applied in this paper.

Cobalt(II) *Complexes*.—Visible and near-i.r. spectral data are in Table 2. The reflectance spectra of all the complexes show a multicomponent band in the visible region, and three bands in the near-i.r. region characteristic of tetrahedral cobalt(II) complexes.[5,6] The spectra are also very similar to those of the cobalt halide complexes of 2-(6-methyl-2-pyridyl)benzothiazole.[7] A large splitting of the ν_2 absorption in the near-i.r. region of the

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spectrum is observed, and it has been suggested [8,9] that this is caused by distortion from ideal tetrahedral symmetry. The magnetic moments of the complexes lie in the range generally found for tetrahedral cobalt(II) complexes.[10] The presence of high-intensity bands in the visible region in the solution spectra are consistent with retention of a tetrahedral structure in solution. However, the band shifts and differences in molar extinction coefficients suggest solvent interactions of the type noted previously.[4,11] The complexes are non-electrolytes in nitromethane and molecular-weight

TABLE 1

Complexes formed by 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dpq) and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)-quinoxaline (dmpq)

Complex		μ_{eff} (B.M.)	Λ_M * Ω^{-1} cm^2 mol^{-1}	M †		Found (%)			Calc. (%)		
				Found	Calc.	M	N	X	M	N	X
L = (dpq)											
$CoCl_2L$	Green	4·64	23·1	450	456	13·0	12·05	15·45	12·9	12·25	15·6
$CoBr_2L$	Green	4·75	18·9	540	545	10·8	9·95	29·35	10·8	10·3	29·35
CoI_2L	Yellow-green	4·78	33·5	650	639	9·3	8·6	39·75	9·25	8·8	39·75
$NiCl_2L$	Yellow-brown	3·31	5·6	480	456	12·8	11·7	15·55	12·9	12·3	15·6
$NiBr_2L$	Yellow-brown	3·32	9·9	530	545	10·85	10·1	29·5	10·8	10·3	29·35
NiI_2L	Red-brown	3·24	18·9	645	639	9·5	8·75	39·7	9·2	8·75	39·8
$CuCl_2L$	Khaki	1·84	20·5	480	461	13·8	12·0	15·55	13·8	12·2	15·4
$CuBr_2L$	Grey-green	1·95				11·8	9·9	29·45	11·55	10·15	29·1
L = (dmpq)											
$CoCl_2L$	Green	4·64	4·3	460	469	12·5	11·7	14·9	12·55	11·9	15·1
$CoBr_2L$	Green	4·74	4·4	570	559	10·4	9·95	28·45	10·55	10·0	28·6
CoI_2L	Yellow-green	4·82	8·3	680	653	8·95	8·7	38·7	9·0	8·6	38·85
$NiCl_2L$	Pale yellow	3·28	4·1	470	469	12·4	11·5	15·25	12·5	11·9	15·1
$NiBr_2L$	Yellow-brown	3·39	6·1	580	559	10·5	9·75	28·65	10·5	10·05	28·6
NiI_2L	Brown	3·37	15·9	610	653	9·3	8·7	39·25	9·0	8·6	38·9
Cu_2Cl_4L	Khaki	1·90				20·55	8·8	22·7	20·85	9·2	23·3

* Measured for 10^{-3}M solutions in nitromethane at 25°. † Measured for 10^{-3}M solutions in dichloroethane at 40°.

TABLE 2

Visible and near-i.r. spectra of the cobalt complexes of 6-methyl-2,3-di(6-methyl-2-pyridyl)quinoxaline (dpq) and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dmpq) in kK

Reflectance spectra

$CoCl_2(dpq)$	18·66, 17·99sh, 17·35, 15·58sh, 14·86, 10·00sh, 7·69, 6·29
$CoBr_2(dpq)$	17·99sh, 17·01sh, 16·61, 16·34sh, 14·79, 10·00, 7·35, 6·06
$CoI_2(dpq)$	16·34sh, 15·53sh, 14·60, 14·01, 13·37sh, 10·87, 9·80, 6·78
$CoCl_2(dmpq)$	22·10sh, 18·76, 17·45, 15·58sh, 15·06, 9·25sh, 7·54, 6·08
$CoBr_2(dmpq)$	20·30sh, 16·69, 15·62sh, 15·06sh, 14·71, 9·52, 7·30, 5·99
$CoI_2(dmpq)$	20·50sh, 16·34, 16·08sh, 15·58sh, 14·60, 13·97sh, 10·00, 6·83, 5·71sh

Solution spectra (molar extinctions in parentheses)

	Ethanol	Acetone	Nitromethane	Dichloroethane
$CoCl_2(dpq)$	17·45(100)	17·53(170)	17·45(170)	16·95(400)
	16·10sh(110)	15·40sh(280)	15·40(300)	15·43sh(660)
	15·05(185)	14·75(350)	15·00(330)	14·87(810)
$CoBr_2(dpq)$	16·75(140)	16·80(335)	16·80(200)	15·57(660)
	14·80(250)	15·00sh(867)	14·90(410)	14·97sh(1370)
		14·70(900)		14·55(1420)
$CoI_2(dpq)$	21·50(1200)			21·05sh(2080)
	15·50(230)	15·50sh(600)	15·60sh(210)	16·10sh(290)
	14·50(325)	14·55(1090)	14·70(280)	15·50sh(510)
	14·00sh(290)	14·00sh(890)	14·10sh(220)	14·47(820)
				13·90sh(670)
$CoCl_2(dmpq)$		17·49(200)	17·55(190)	17·45(220)
		15·35(320)	15·60sh(330)	15·40(350)
		14·85(460)	15·10(370)	14·85(420)
$CoBr_2(dmpq)$		16·22(240)	16·35(240)	16·25(275)
		14·87sh(490)	15·02(500)	15·02sh(540)
		14·65(500)		14·70(550)
$CoI_2(dmpq)$		21·50sh(3890)	15·55sh(400)	16·10sh(170)
		16·05sh(500)	14·65(605)	15·52sh(275)
		15·55sh(830)	14·00sh(485)	14·55(445)
		14·48(1420)		13·90sh(370)
		13·95sh(1200)		

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determinations in dichloroethane show that they are monomeric. Thus the only possible structure for the cobalt complexes of dpq and dmpq is monomeric tetrahedral, involving bidentate non-bridging ligand molecules.

Nickel(II) *Complexes*.—The spectral data for the nickel complexes of dpq and dmpq are in Table 3. The complexes $NiCl_2$(dpq), $NiBr_2$(dpq), and $NiBr_2$(dmpq) have very similar reflectance spectra. The two nickel iodide complexes have similar reflectance spectra, and although these spectra differ in the visible region from those of the above three complexes they show similar bands in the near-i.r. region. The reflectance spectra of these complexes are very different from those expected for octahedral or square planar nickel(II) complexes.[12] However, they are similar to those of distorted tetrahedral nickel(II) complexes of substituted pyridines and related compounds.[13–15] Although the magnetic moments of the complexes are lower than those expected for tetrahedral nickel(II) complexes,[10] many distorted tetrahedral nickel(II) complexes have magnetic moments of the same order.[14,16] The reflectance spectrum of $NiCl_2$(dmpq) is very different from those of the other nickel complexes, but is very similar to those of the nickel complexes of 2,3-di-(6-methyl-2-pyridyl)quinoxaline [4] and to those of other tetragonally distorted octahedral nickel(II) complexes.[17,18] The magnetic moment of $NiCl_2$(dmpq) (3·28 B.M.) is in the range expected for tetragonally distorted nickel(II) complexes.[19] All the nickel complexes of dpq and dmpq readily dissolve in organic solvents, and, with the exception of $NiCl_2$(dmpq), the solution spectra closely resemble the reflectance spectra. This strongly suggests that with the exception of $NiCl_2$(dmpq) the nickel complexes are unchanged on dissolution. The species in solution are non-electrolytes, and molecular-weight measurements in dichloroethane show that they are monomeric. From the above evidence a monomeric distorted tetrahedral structure is assigned to all the nickel complexes, except $NiCl_2$(dmpq), the ligand being bidentate and non-bridging. Although the solution spectra of $NiCl_2$(dmpq) are different from the reflectance spectrum, they are very similar to the spectra of $NiCl_2$(dpq), $NiBr_2$(dpq), and $NiBr_2$(dmpq). Thus a distorted tetrahedral species is present in solution, and molecular-weight measurements in dichloroethane confirm the presence of a monomeric complex. However, since solid $NiCl_2$(dmpq) clearly has a distorted octahedral structure, the stoicheiometry requires that it must be polymeric, dissociating to the tetrahedral monomer in solution. This is exactly analogous to the nickel

TABLE 3

Visible and near-i.r. spectra of the nickel and copper complexes of 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dpq) and 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dmpq) in kK

Reflectance spectra

$NiCl_2$(dpq)	21·00, 18·87sh, 16·72, 13·40sh, 12·05, 11·49, 10·10, 8·13sh
$NiBr_2$(dpq)	19·61, 16·78sh, 11·11, 9·90, 7·69sh
NiI_2(dpq)	21·50br, 14·71, 10·42, 9·80sh, 7·57sh
$CuCl_2$(dpq)	20·16sh, 13·40sh, 11·42
$CuBr_2$(dpq)	15·40sh,vbr
$NiCl_2$(dpq)	23·05sh, 19·53sh, 13·97br, 9·52, 6·33
$NiBr_2$(dpq)	20·24, 16·89, 16·29sh, 10·87sh, 9·52, 7·63
NiI_2(dmpq)	20·30sh, 15·04, 10·31, 9·61sh, 7·87sh
Cu_2Cl_4(dmpq)	19·61, 12·50

Solution spectra (molar extinctions in parentheses)

	Ethanol	Acetone	Nitromethane	Dichloroethane
$NiCl_2$(dpq)	14·00(14)	20·60(140) 16·40(13·8)	20·80(80)	20·55(140) 16·10(13)
$NiBr_2$(dpq)	20·50sh(27) 14·00(13)	19·85(210) 16·00(15)	20·10(120)	19·80(220) 16·80sh(30) 15·80sh(20)
NiI_2(dpq)	21·00sh(285) 15·00(20)	21·50sh(3800) 15·10(150)	21·45sh(1180) 15·50(60)	20·80sh(860) 14·95(150)
$CuCl_2$(dpq)	19·40(450) 16·50sh(140)	21·30sh(600) 20·00(570)	21·50(410)	
$NiCl_2$(dmpq)		20·65(140) 16·20(17)	20·70(135) 16·25(10)	20·70(170) 16·50(20)
$NiBr_2$(dmpq)		19·87(250) 16·90sh(30) 16·00(23)	19·95(190) 16·00(12)	19·90(310) 16·88sh(31) 16·00(20)
NiI_2(dmpq)		21·60sh(630) 15·10(140)	21·50sh(1700) 15·50(95)	21·50sh(660) 15·05(140)

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complexes of 2,3-di-(6-methyl-2-pyridyl)quinoxaline,[4] and a similar structure is assigned to $NiCl_2$(dmpq), involving bis-bidentate bridging ligand.

Copper(II) *Complexes*.—There is abundant evidence [20-23] that substituent groups adjacent to a heterocyclic co-ordination site frequently have a strong tendency to inhibit square planar co-ordination at copper-(II). However, in this case a square planar geometry is tentatively assigned to $CuCl_2$(dpq) and $CuCl_4$(dmpq) on the basis of their reflectance spectra (Table 3), subject to recently-expressed uncertainties.[24] The complex $CuCl_2$(dpq) is readily soluble in organic solvents, but the solution spectra are very different from the reflectance spectrum. However, there are strong resemblances between the solution spectra of $CuCl_2$(dpq) and those of the copper complexes of 2,3-di-(6-methyl-2-pyridyl)-quinoxaline.[4] A monomeric tetrahedral structure was assigned [4] to the latter complexes in solution, and it is considered that CuCl(dpq) has an analogous structure in solution. In view of the high molar extinction coefficients, the bands in the visible region of the solution spectra of $CuCl_2$(dpq) are probably associated with a charge-transfer transition, analogous to the spectra published [25] for some other sterically hindered copper halide complexes. The presence of a monomeric species in solution is confirmed by molecular-weight determinations in dichloroethane. Although the solution properties of $CuCl_2$(dpq) do not reflect on the nature of the solid complex, the most reasonable structure is monomeric, in which the ligand is bidentate and non-bridging. The complex Cu_2Cl_4(dmpq) is insoluble in organic solvents. A polymeric structure cannot be assigned to this complex since such a structure would involve both halogen and ligand bridging, and it has been shown [2] that it is sterically not possible for the ligand to bridge halogen-bridged polymer chains. Also, the similarities of the reflectance spectra of Cu_2Cl_4(dmpq) to that of $CuCl_2$(dpq) suggest that the former complex is dimeric, the ligand being bis-bidentate bridging and the halogen atoms being terminal. The data for $CuBr_2$-(dpq) are very inconclusive, and no structural deductions can be made. The reflectance spectrum shows high absorption throughout the visible region, and the only feature is a very broad, ill-defined shoulder *ca.* 15·4 kK. The complex is insoluble in organic solvents, and no definite information can be obtained from the i.r. spectrum of the complex. Attempts to prepare the copper bromide complex with dmpq resulted in a very impure product.

I.r. Spectra.—The i.r. spectra of the ligands and some of their complexes are in Table 4. The cobalt complexes of dpq and $CuCl_2$(dpq) have similar i.r. spectra, and it is inferred that the ligand co-ordinates in the same way in these complexes. The nickel complexes of dpq all have similar i.r. spectra but they show some differences from those of the cobalt complexes. The bands at 1475 and 1026 cm^{-1} in the spectra of the cobalt complexes are split in those of the nickel complexes. Three strong bands at 1170, 1160, and 1155 cm^{-1} in the spectra of the nickel complexes are weak in those of the cobalt complexes. There are differences in the region 830—770 cm^{-1}, the cobalt complexes showing five bands and the nickel complexes showing only four. Since the electronic spectra and magnetic data indicate that the cobalt and nickel complexes have similar structures, and the same mode of ligand co-ordination, it is assumed that the differences in the i.r. spectra arise through distortions from regular structures. The i.r. spectrum

TABLE 4

I.r. spectra of 6-methyl-2,3-di-(6-methyl-2-pyridyl)quinoxaline (dpq), 6,7-dimethyl-2,3-di-(6-methyl-2-pyridyl)-quinoxaline (dmpq) and their complexes (1650—550 cm^{-1}); all bands strong or medium unless otherwise stated

dpq	1623w, 1590, 1572, 1555, 1546sh, 1506w, 1493, 1462, 1412sh,w, 1404w, 1383, 1372, 1351, 1248w, 1242w, 1159, 1145, 1111sh, 1103, 1094, 1081, 1043, 995, 983sh, 975w, 928w, 892w, 877w, 847w, 833, 820, 807, 794, 790, 786, 758, 747, 741w, 726w, 683w, 671w, 668w, 629w, 622w, 601w, 586w, 577, 562
All complexes	*1625 ± 4, 1608 ± 5, *1596 ± 1, *1576 ± 1, *1498 ± 1, 1475 ± 2, *1462 ± 2, 1431 ± 2, *1382 ± 4, *1357 ± 4, 1319 ± 2, 1283 ± 5w, *1257 ± 4w, *1231 ± 3w, 1214 ± 3, 1185 ± 3, *1161 ± 2, 1153 ± 3, 1119 ± 5, *1107 ± 3, *1093 ± 3, 1053 ± 5, *1039 ± 2sh, 1026 ± 4, 1002 ± 3w, *995 ± 2, *887 ± 4w, *851 ± 3, *830 ± 4, *807 ± 3, *795 ± 5, *784 ± 2, *759 ± 2, *747 ± 3, 700 ± 5, *681 ± 3w, *630 ± 3, *600 ± 2, *585 ± 1
$CoCl_2L$	1567sh, *1546w, 1534w, *1508w, *1401w, 1333w, 1290sh,w, 1266w, 1245w, 1172, 920w, *877w, 813sh, 811, 753, *740w, *668w, 646w, *621w, 617w
$NiCl_2L$	1531w, *1401, *1377, 1269, 1168, 1125, 1048w, 901, 862w, 815, 802, 734, 724w, 668w, 648w, 619w, 593sh, 570w, 548w
dmpq	1626w, 1590, 1575, 1553, 1522w, 1508w, 1486, 1464, 1453, 1429, 1401, 1389w, 1376, 1364w, 1353, 1297w, 1255, 1242, 1222, 1198, 1159, 1153, 1105, 1094, 1081, 1048, 1036w, 1026, 1004, 996, 986, 975w, 919, 908w, 901, 884w, 871, 856, 827, 819w, 803, 791, 764, 751, 739, 725, 678, 670, 627, 624, 589, 576, 551
All complexes	*1624 ± 2w, 1606 ± 1, *1577 ± 3, 1473 ± 2, *1433 ± 4, *1402 ± 2w, *1379 ± 2, *1357 ± 4, 1280 ± 2, *1259 ± 4w, 1232 ± 2, 1213 ± 4, 1170 ± 2, 1129 ± 2, *1109 ± 3w, 1058 ± 2, *1024 ± 4, *1007 ± 3, *996 ± 2, *893 ± 4w, *822 ± 2, *808 ± 3, *788 ± 3w, *751 ± 4, *737 ± 5, 698 ± 2w
$CoCl_2L$	*1597, *1550w, 1538w, *1515w, *1481, *1302w, *1202, *1166, *1095w, 1042w, *917w, *875w, *757, *723w, 648w, 635w, *626w, 599w

* Bands due to ligand.

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of $CuBr_2$(dpq) shows differences from those of the other complexes of dpq, but no information concerning the ligand co-ordination can be gained. All the complexes of dmpq have similar i.r. spectra, and it is concluded that the ligand co-ordinates in the same way in all these complexes.

EXPERIMENTAL

Magnetic and spectral measurements were made as before.[26] I.r. spectra were recorded as potassium bromide discs using Grubb–Parsons Spectromaster and Unicam SP200 instruments. Molecular-weight measurements were made in dichloroethane using a Perkin-Elmer–Hitachi model 115 vapour-pressure osmometer, and conductivity measurements were recorded at 25 °C using a Lock Type MCB2 conductivity bridge, the solutions in nitromethane being 10^{-3}M. Solvents were dried by standard methods and fractionated before use.

6-*Methyl*-2,3-*di*-(6-*methyl*-2-*pyridyl*)*quinoxaline* was prepared by heating equimolar quantities of 1,2-di-(6-methyl-2-pyridyl)ethane-1,2-dione and 3,4-diaminotoluene in refluxing ethanol for 6 h. The solvent was removed and the product was recrystallised from aqueous ethanol using charcoal. The white crystalline product was dried at 100° (Found: C, 76·9; H, 5·7; N, 16·95. Calc. for $C_{21}H_{18}N_4$: C, 77·25; H, 5·55; N, 17·15%). It had m.p. 162°.

6,7-*Dimethyl*-2,3-*di*-(6-*methyl*-2-*pyridyl*)*quinoxaline* was prepared as above using 1,2-di-(6-methyl-2-pyridyl)ethane-1,2-dione and 4,5-dimethyl-1,2-phenylenediamine (Found: C, 77·45; H, 5·95; N, 16·3. Calc. for $C_{22}H_{20}N_4$: C, 77·6; H, 5·9; N, 16·45%). It had m.p. 171°.

The complexes were prepared by heating equimolar quantities of the metal halides with the appropriate ligand in refluxing ethanol for 2 h. After removal of some of the solvent the precipitated complexes were filtered off, washed thoroughly with ethanol, and dried at 110°.

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