Transition Metal Complexes of Substituted 2,2'-Biquinolines. Part 1. The Crystal and Molecular Structures of [8,8'-Bis(aminomethyl)-2,2'-biquinoline]dichloromanganese(II) and [8,8'-Bis(aminomethyl)-2,2'-biquinoline]chlorocopper(II) Chloride†

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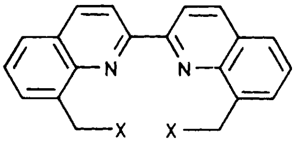
The potentially quadridentate ligand, 8,8'-bis(aminomethyl)-2,2'-biquinoline (L^1) was prepared in 41% overall yield from 8,8'-dimethyl-2,2'-biquinoline by conversion to the 8,8'-bis(bromomethyl) derivative with *N*-bromosuccinimide, followed by reaction with NaN_3 and reduction with $LiAlH_4$. The complexes $[Cu(L^1)Cl]Cl$ and $[Mn(L^1)Cl_2]$ have been prepared and structurally characterised. The copper is in a distorted five-co-ordinate square-based pyramidal environment in $[Cu(L^1)Cl]Cl$ with the co-ordinated chloride occupying the axial site; in contrast, the manganese complex exhibits a distorted octahedral geometry about the metal.

The polydentate ligands 2,2'-bipyridine (bipy) and 2,2':6',2''-terpyridine (terpy) have played major roles in the development of 'classical' co-ordination chemistry.[1,2] In contrast, the benzo-analogue, 2,2'-biquinoline (L^2) has received relatively scant attention.[3] This is due, in part, to the synthetic difficulties associated with the preparation of 2,2'-biquinoline and its derivatives. We have reported the incorporation of 2,2'-bipyridine and 2,2':6',2''-terpyridine moieties into macrocyclic ligands, and wished to extend our studies to the incorporation of 2,2'-biquinolines.[4] A number of recent reports have demonstrated the novel properties of such macrocyclic systems,[5] and we report herein the synthesis and co-ordination chemistry of a key intermediate in the preparation of such macrocycles, 8,8'-bis(aminomethyl)-2,2'-biquinoline (L^1).

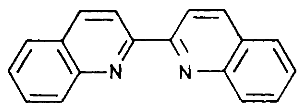
Results and Discussion

Our initial aim was the synthesis of 8,8'-bis(aminomethyl)-2,2'-biquinoline (L^1), which we hoped would undergo template condensation with dicarbonyls to yield macrocyclic ligands or complexes. We considered a number of strategies for the synthesis of L^1, and finally developed a route in which the fusion of the two quinoline rings was achieved in an early step.

8-Methylquinoline was converted to 8,8'-dimethyl-2,2'-biquinoline (L^3) in high yield by oxidative dimerisation over 5% palladium–charcoal.[6] Although individual pass yields of 12% could be obtained, the reaction was found to be critically dependent upon the batch of catalyst being used. In our hands, the best yields were only 70% of those reported previously.[6] The 8,8'-dimethyl compound, L^3, was converted to 8,8'-bis(bromomethyl)-2,2'-biquinoline (L^4) by reaction with two equivalents of *N*-bromosuccinimide in tetrachloromethane. The compound was obtained as a white solid in 85% yield. The reaction is readily monitored by ^1H n.m.r. spectroscopy; the singlet at δ 2.42 due to the methyl groups of L^3 is replaced by a new singlet a δ 5.38, assigned to the benzylic methylene functionality. The mass spectrum of the compound exhibits parent ion peaks at *m*/*z* 440, 442, and 444 in the expected 1:2:1 ratio of intensities.



X
L^1, NH_2
L^3, H
L^4, Br
L^5, N_3



L^2

Attempts to convert the bromomethyl derivative to the amine directly, by reaction with ammonia or by a Gabriel reaction with potassium phthalimide were unsuccessful. However, reaction with an ethanolic solution of sodium azide resulted in the formation of the bis(azidomethyl) derivative, L^5, in good yield [$\nu(N_3)$ at 2 111 cm^{-1} [7]].

The desired amino compound, L^1, was obtained in 60% yield by the reduction of L^5 with $LiAlH_4$ in diethyl ether. The product exhibits a molecular ion peak at *m*/*z* 314 in the mass spectrum. The ^1H n.m.r. spectrum exhibited broad resonances centred at δ 2.9 ascribed to the amino protons, and a sharp singlet due to the methyl protons at δ 4.54.

The reaction of L^1 with zinc chloride in methanol resulted in the formation of a pale yellow solution, from which the complex $[Zn(L^1)(H_2O)_2][PF_6]_2$ could be obtained as an orange solid. The ^1H n.m.r. spectrum of this complex (Figure 1) exhibited a single methylene resonance indicating that the molecular C_2 symmetry is retained in the complex. We suggest that the complex possesses octahedral geometry, with zinc binding the four nitrogen donors of L^1 in the equatorial plane, and with the axial sites occupied by the water molecules.

The reaction of nickel(II) nitrate with a methanolic solution of L^1 resulted in the formation of a pale brown solution, from which crystals of the brown complex $[Ni(L^1)(H_2O)_2][NO_3]_2$ could be obtained after concentration and cooling. The complex is paramagnetic ($\mu_{eff.}$ = 2.95, room temperature) which precludes formulation as a square-planar $[Ni(L^1)]^{2+}$ species. The ligand L^1 cannot distort to impose a tetrahedral geometry upon a metal ion. The magnetic moment is consistent with an octahedral geometry about the metal, with the axial sites

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

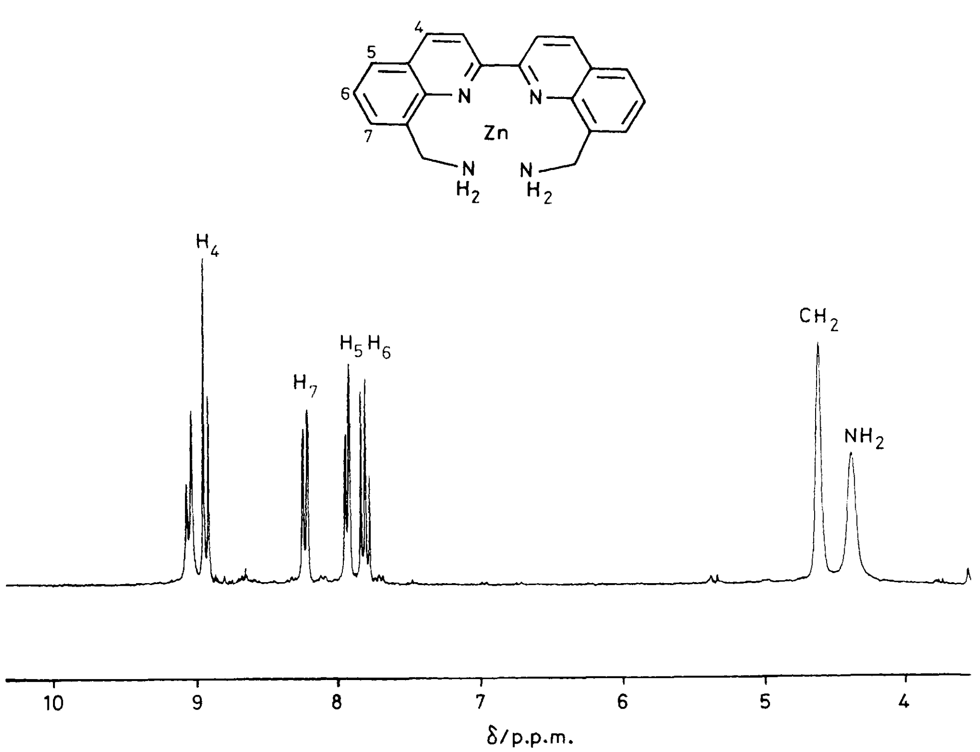

Figure 1. 250-MHz ^1H N.m.r. spectrum of the complex $[Zn(L^1)(H_2O)_2][PF_6]_2$

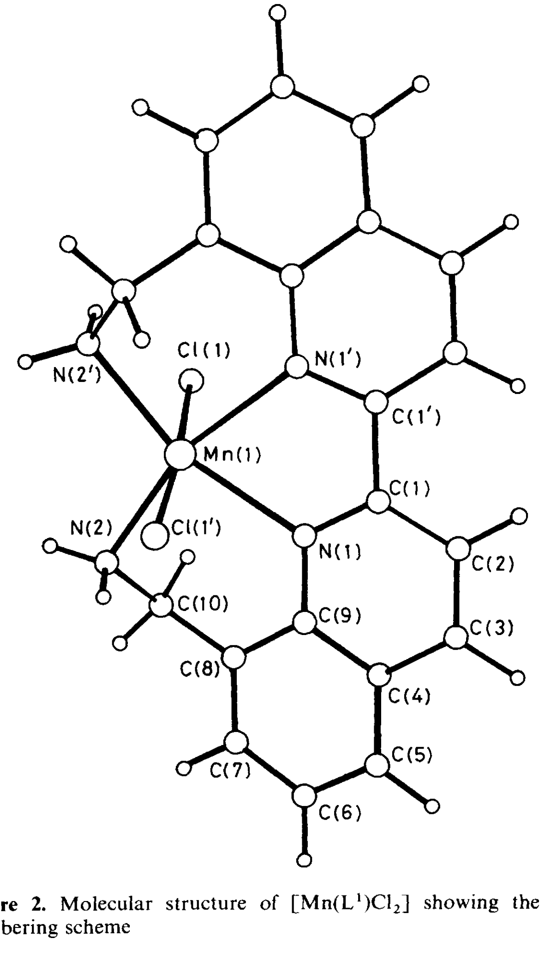

Figure 2. Molecular structure of $[Mn(L^1)Cl_2]$ showing the atom numbering scheme

occupied by water or possibly nitrate ion. Attempts to characterise this complex structurally were unsuccessful, owing to decomposition in the *X*-ray beam. Accordingly, we cannot eliminate the possibility of a five-co-ordinate square-based pyramidal geometry, although the magnetic properties are not in accord with this.

Treatment of L^1 with methanolic $[Co(H_2O)_6][BF_4]_2$ in an inert atmosphere resulted in the formation of an extremely air-sensitive deep purple solution. Concentration of this solution yielded red needles of the very dioxygen-sensitive complex $[Co(L^1)][BF_4]_2$. We have demonstrated this complex to be an active carrier for dioxygen.[8] A similar, very air-sensitive, purple solution was also obtained upon reaction of L^1 with methanolic solutions of iron(II) chloride. Addition of ammonium hexafluorophosphate to the purple solution led to the deposition of green crystals of $[Fe(L^1)(H_2O)_2][PF_6]_2$. No complexes were isolated from the attempted reaction of L^1 with chromium(III) or vanadium(III) salts in methanol.

A brown crystalline complex $[Mn(L^1)Cl_2]$ was obtained from the reaction of manganese(II) chloride with L^1 in methanol. The complex was paramagnetic (μ_{eff} = 5.93) with a moment very close to the value of 5.92 expected from the spin-only formula for a high-spin d^5 ion ($^6A_{1g}$ ground term) in an octahedral environment. *X*-Ray quality crystals were obtained by vapour diffusion of diethyl ether into a methanol solution of the complex, and the crystal and molecular structure was determined. The molecular structure of the complex is shown in Figure 2. Selected bond parameters for the complex $[Mn(L^1)Cl_2]$ are listed in Table 1. The molecule sits on a crystallographic two-fold axis which passes through the Mn atom. The metal is in an approximately octahedral environment, with the N_4 donor set of the ligand occupying the equatorial sites and the chloride ions the axial sites. The Cl–Mn–Cl angle is 175.7(1)°, indicating a slight distortion of the axial chlorides. The chlorides are distorted towards the two amino groups of the ligand, and it is possible that this represents a weak $-NH \cdots Cl$ hydrogen bonding interaction [H(11B)–Cl, 2.35(2) Å]. The manganese is displaced towards the amino nitrogen donor atoms [Mn–N(2), 2.211(6) Å] away from the quinoline nitrogen [Mn–N(1), 2.285(5) Å]. This closely resembles the Mn–N distance of 2.235 Å reported for the complex $[(\mathrm{L}^2)\mathrm{MnCl}(\mu\text{-Cl})_2\mathrm{MnCl}(\mathrm{L}^2)]$.[9] The bite of the N_4 donor ligand is such that it cannot adopt a regular square-planar donor set, with all N–Mn–N angles at 90°. The observed distortion results in a lower bond angle to the two quinoline nitrogen donors N(1)–Mn–N(1A), 74.8(3)° and an increased angle to the amine nitrogens N(2)–Mn–N(2A), 112.0(3)°. The two quinoline systems are not coplanar, but subtend a dihedral angle of 37.4°. This is larger than the dihedral angle in $[(\mathrm{L}^2)\mathrm{ClMn}(\mu\text{-Cl})_2\mathrm{MnCl}(\mathrm{L}^2)]$ of 11.3°,[9] but serves to minimize the unfavourable van der Waals interactions between H(2) and H(2A), which have a non-bonded contact of 2.09(2) Å. The phenyl and pyridyl rings of each quinoline are at an angle of 5.0° to each other, resulting in the 'banana' distortion of the ligand observed previously in 2,2′-biquinoline complexes.[9,10] All other bond lengths and angles within the organic fragment are unremarkable, and closely resemble those of the free ligand, 2,2′-biquinoline.[11]

Treatment of a solution of $[\mathrm{Mn}(\mathrm{L}^1)\mathrm{Cl}_2]$ in warm water with ammonium hexafluorophosphate led to the precipitation of $[\mathrm{Mn}(\mathrm{L}^1)(\mathrm{H_2O})_2][\mathrm{PF}_6]_2$ as white plates. This complex is also paramagnetic, and exhibits an e.s.r. spectrum at 77 K in a frozen water glass. The signal is near isotropic, and shows a signal at $g_{\text{av.}} = 2.110$, with coupling to the ^{55}Mn ($I = \frac{7}{2}$) nucleus, with $A = 30$ G.

The reaction of L^1 with a methanolic solution of copper(II) chloride resulted in the formation of a dark green solution, from which a very dark green solid with a purple dichroism separated upon cooling. Recrystallisation from warm water gave large black-green crystals. The complex is paramagnetic with a room temperature $\mu_{\text{eff.}}$ of 1.77. The e.s.r. spectrum of a frozen methanol glass at 77 K exhibits an anisotropic signal with $g_{\parallel} = 2.206$ and $g_{\perp} = 2.075$. No hyperfine coupling to ^{63}Cu, ^{65}Cu, or ^{14}N could be observed under these conditions. The crystal and molecular structure of the complex was determined.

The crystal structure revealed the presence of a five-coordinate $[\mathrm{Cu}(\mathrm{L}^1)\mathrm{Cl}]^+$ cation and a chloride anion; the molecular structure of the cation is shown in Figure 3. Selected bond lengths and angles are listed in Table 2. The copper is bonded to the four nitrogen donors of the ligand, which form the basal plane of a square-based pyramid, in which the axial site is occupied by a chloride. The remaining chloride ion is not coordinated to the metal, but is involved in a hydrogen-bonding network with lattice water and the amino group protons.

Table 1. Selected bond lengths (Å) and angles (°) for $[\mathrm{Mn}(\mathrm{L}^1)\mathrm{Cl}_2]$

Mn(1)–N(1)	2.285(5)	C(3)–C(4)	1.397(10)
Mn(1)–N(2)	2.211(6)	C(4)–C(5)	1.436(10)
Mn(1)–Cl(1)	2.532(2)	C(4)–C(9)	1.419(9)
N(1)–C(9)	1.374(8)	C(5)–C(6)	1.362(11)
C(9)–C(8)	1.423(9)	C(6)–C(7)	1.405(11)
C(8)–C(10)	1.502(10)	C(7)–C(8)	1.385(10)
C(10)–N(2)	1.469(9)	C(1)–N(1)	1.318(8)
C(1)–C(2)	1.407(9)	C(1)–C(1A)	1.502(12)
C(2)–C(3)	1.363(10)		
N(1)–Mn(1)–C(1)	94.3(1)	C(9)–C(4)–C(5)	119.4(7)
N(2)–Mn(1)–Cl(1)	91.1(2)	C(6)–C(5)–C(4)	119.9(7)
N(2)–Mn(1)–N(1)	86.6(2)	C(7)–C(6)–C(5)	120.2(7)
C(1)–N(1)–Mn(1)	112.4(4)	C(8)–C(7)–C(6)	122.5(7)
C(9)–N(1)–Mn(1)	125.0(4)	C(9)–C(8)–C(7)	118.1(7)
C(9)–N(1)–C(1)	119.2(6)	C(10)–C(8)–C(7)	119.3(7)
N(1)–Mn(1)–N(1A)	74.8(3)	C(10)–C(8)–C(9)	122.4(6)
C(2)–C(1)–N(1)	123.5(6)	C(4)–C(9)–N(1)	119.5(6)
C(3)–C(2)–C(1)	118.6(7)	C(8)–C(9)–N(1)	120.6(6)
C(4)–C(3)–C(2)	119.3(7)	C(8)–C(9)–C(4)	119.9(6)
C(5)–C(4)–C(3)	120.9(7)	N(2)–C(10)–C(8)	114.1(6)
C(9)–C(4)–C(3)	119.6(6)	C(10)–N(2)–Mn(1)	111.6(4)

Table 3. Elemental analysis for new ligands and complexes

	Found (%)			Calc. (%)		
Compound	C	H	N	C	H	N
L^1	76.3	5.5	17.6	76.4	5.7	17.8
L^4	54.8	3.0	6.2	54.5	3.2	6.4
$[\mathrm{Zn}(\mathrm{L}^1)(\mathrm{H_2O})_2][\mathrm{PF}_6]$	34.2	3.0	8.2	34.0	3.1	7.9
$[\mathrm{Ni}(\mathrm{L}^1)(\mathrm{H_2O})_2][\mathrm{NO}_3]_2$	44.9	4.0	16.0	45.0	4.1	15.8
$[\mathrm{Co}(\mathrm{L}^1)][\mathrm{BF}_4]_2\cdot\mathrm{H_2O}$	42.9	3.2	9.8	42.6	3.5	9.6
$[\mathrm{Mn}(\mathrm{L}^1)\mathrm{Cl}_2]$	54.7	4.2	12.8	54.6	4.1	12.7
$[\mathrm{Cu}(\mathrm{L}^1)\mathrm{Cl}]\mathrm{Cl}\cdot2\mathrm{H_2O}$	49.3	4.7	11.3	49.5	4.5	11.5

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Cu}(\mathrm{L}^1)\mathrm{Cl}]\mathrm{Cl}$

N(1)–Cu(1)	2.006(5)	C(8)–N(3)	1.489(12)	C(7)–C(4)	1.408(16)	C(19)–C(13)	1.419(15)
N(2)–Cu(1)	2.020(8)	C(17)–N(4)	1.482(12)	C(9)–C(5)	1.362(18)	C(15)–C(14)	1.383(13)
N(3)–Cu(1)	1.998(9)	C(3)–C(1)	1.416(9)	C(8)–C(6)	1.505(10)	C(17)–C(14)	1.501(14)
N(4)–Cu(1)	1.978(5)	C(10)–C(1)	1.494(12)	C(20)–C(6)	1.383(14)	C(16)–C(15)	1.404(18)
Cl(1)–Cu(1)	2.633(2)	C(4)–C(2)	1.428(9)	C(9)–C(20)	1.389(11)	C(18)–C(16)	1.351(12)
C(1)–N(1)	1.333(12)	C(6)–C(2)	1.425(14)	C(10)–C(11)	1.408(15)	C(19)–C(18)	1.419(14)
C(2)–N(1)	1.358(11)	C(7)–C(3)	1.359(15)	C(12)–C(11)	1.354(15)	Cu(1)–Cl(1)	2.633(2)
C(10)–N(2)	1.324(8)	C(2)–C(4)	1.428(9)	C(19)–C(12)	1.407(10)		
C(13)–N(2)	1.370(10)	C(5)–C(4)	1.413(14)	C(13)–C(14)	1.425(9)		
N(2)–Cu(1)–N(1)	82.8(3)	C(13)–N(2)–Cu(1)	127.9(5)	C(9)–C(5)–C(4)	119.5(7)	C(19)–C(13)–N(2)	120.6(6)
N(3)–Cu(1)–N(1)	90.0(3)	C(13)–N(2)–C(10)	119.2(8)	C(8)–C(6)–C(2)	124.0(8)	C(19)–C(13)–C(14)	119.5(8)
N(3)–Cu(1)–N(2)	158.3(3)	C(8)–N(3)–Cu(1)	110.8(5)	C(20)–C(6)–C(2)	118.2(7)	C(15)–C(14)–C(13)	117.7(9)
N(4)–Cu(1)–N(1)	172.3(3)	C(17)–N(4)–Cu(1)	113.6(4)	C(20)–C(6)–C(8)	117.6(10)	C(17)–C(14)–C(13)	123.2(8)
N(4)–Cu(1)–N(2)	92.7(3)	C(3)–C(1)–N(1)	115.9(6)	C(10)–C(7)–C(3)	120.3(7)	C(17)–C(14)–C(15)	118.5(7)
N(4)–Cu(1)–N(3)	92.0(3)	C(10)–C(1)–C(3)	122.0(9)	C(6)–C(8)–N(3)	112.8(8)	C(16)–C(15)–C(14)	122.6(7)
Cl(1)–Cu(1)–N(1)	93.0(2)	C(4)–C(2)–N(1)	119.9(8)	C(20)–C(9)–C(5)	119.7(10)	C(18)–C(16)–C(15)	120.2(10)
Cl(1)–Cu(1)–N(2)	98.2(2)	C(6)–C(2)–N(1)	122.1(6)	C(10)–C(10)–N(2)	116.0(8)	C(14)–C(17)–N(4)	112.8(7)
Cl(1)–Cu(1)–N(3)	102.6(2)	C(6)–C(2)–C(4)	117.9(8)	C(11)–C(10)–N(2)	123.2(8)	C(19)–C(18)–C(16)	120.0(11)
Cl(1)–Cu(1)–N(4)	93.9(2)	C(7)–C(3)–C(1)	118.7(9)	C(11)–C(10)–C(1)	120.9(6)	C(13)–C(19)–C(12)	118.0(9)
C(1)–N(1)–Cu(1)	112.4(5)	C(5)–C(4)–C(2)	121.2(9)	C(12)–C(11)–C(10)	118.5(7)	C(18)–C(19)–C(12)	122.1(10)
C(2)–N(1)–Cu(1)	126.9(6)	C(7)–C(4)–C(2)	118.4(8)	C(19)–C(12)–C(11)	120.5(11)	C(18)–C(19)–C(13)	119.9(7)
C(2)–N(1)–C(1)	120.6(6)	C(7)–C(4)–C(5)	120.4(7)	C(17)–C(13)–N(2)	119.8(9)	C(9)–C(20)–C(6)	123.4(11)
C(10)–N(2)–Cu(1)	112.2(6)	C(9)–C(5)–C(4)	119.5(7)				

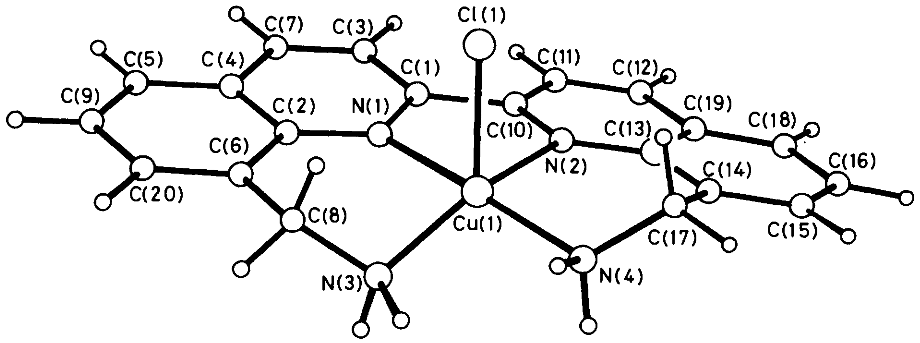

Figure 3. Molecular structure of the $[Cu(L^1)Cl]^+$ cation showing the atom numbering scheme

The Cu(1)–Cl(1) bond distance of 2.633(2) Å is similar to, but slightly shorter than such bonds in other five-co-ordinate copper(II) complexes.[12] The Cu–N(quinoline) distances are slightly, but not significantly, larger than the Cu–N(amine) distances, the Cu–N_{av} distance of 2.00(1) Å closely resembles those in $[Cu(terpy)Cl_2]$ (2.02 Å),[13] $[Cu(terpy)Cl_2]\cdot H_2O$ (2.01 Å),[13] and $[\{Cu_3(L^2)_2(CN)_3\}_n]$ (2.096 Å).[14] The dihedral angle between the two pyridyl rings is 9.1°, the twisting within the quinoline rings is considerably less than in the manganese complex, with the phenyl ring making an angle of 1.4° with the pyridyl ring. The non-bonded contact between H(3) and H(11) is 1.978(12) Å. The copper lies 0.24 Å above the approximate square plane of nitrogen atoms.

Experimental

Infrared spectra were recorded as Nujol mulls supported between potassium bromide discs using Perkin-Elmer 983 or 1700 spectrophotometers. E.s.r. spectra were recorded on a Varian E109 spectrometer (*X*-band). N.m.r. spectra were recorded on Brüker WP80, WM250, or AM400 spectrometers.

8-Methylquinoline and 5% palladium-on-charcoal were used as supplied by the Aldrich Chemical Company. 8,8′-Dimethyl-2,2′-biquinoline was prepared by the literature method.[6] Elemental analyses are given in Table 3.

Syntheses.—*8,8′-Bis(bromomethyl)-2,2′-biquinoline.* 8,8′-Dimethyl-2,2′-biquinoline (2.50 g, 8.8 mmol), *N*-bromosuccinimide (3.13 g, 18.0 mmol), and benzoyl peroxide (0.30 g) were heated to reflux in CCl_4 (400 cm^3) for 4 h. The suspension obtained was concentrated *in vacuo* and the white solid collected by filtration. The solid was boiled with water (150 cm^3) for 15 min, collected by filtration, washed with hot water (150 cm^3), and air dried to yield 8,8′-bis(bromomethyl)-2,2′-biquinoline (3.3 g, 85%).

8,8′-Bis(azidomethyl)-2,2′-biquinoline. 8,8′-Bis(bromomethyl)-2,2′-biquinoline (3.0 g, 6.8 mmol) in boiling ethanol (300 cm^3) was treated with NaN_3 (1.1 g, 17 mmol) and the solution heated to reflux for 3 h. The solution was filtered hot and cooled, whereupon the 8,8′-bis(azidomethyl)-2,2′-biquinoline separated as a white solid (2.05 g, 80%).

8,8′-Bis(aminomethyl)-2,2′-biquinoline. 8,8′-Bis(azidomethyl)-2,2′-biquinoline (0.5 g, 1.4 mmol) was suspended in dry diethyl ether (50 cm^3) and cautiously treated with $LiAlH_4$ (0.1 g, 2.6 mmol). The reaction mixture was stirred for 1 h. The suspension was cautiously quenched by the addition of an ice–water mixture (200 cm^3), and extracted with diethyl ether (2 × 100 cm^3) and chloroform (3 × 200 cm^3). The combined extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield 8,8′-bis(aminomethyl)-2,2′-biquinoline (0.28 g, 60%).

Table 4. Atomic co-ordinates for $[Mn(L^1)Cl_2]$

Atom	*x*	*y*	*z*
Mn(1)	2 500	1 923(1)	5 000
Cl(1)	−394(2)	1 842(2)	5 574(1)
N(1)	1 793(7)	3 478(4)	4 374(3)
C(1)	2 319(8)	4 448(5)	4 638(3)
C(2)	2 571(9)	5 460(6)	4 276(4)
C(3)	2 317(9)	5 434(6)	3 614(4)
C(4)	1 773(9)	4 416(6)	3 318(3)
C(5)	1 444(10)	4 363(7)	2 625(4)
C(6)	753(10)	3 397(7)	2 358(4)
C(7)	366(10)	2 453(7)	2 758(4)
C(8)	670(9)	2 451(6)	3 428(3)
C(9)	1 419(9)	3 445(6)	3 715(3)
C(10)	102(9)	1 442(6)	3 832(4)
N(2)	1 510(9)	864(5)	4 183(3)

Preparation of Metal Complexes.—$[Zn(L^1)(H_2O)_2][PF_6]_2$. Zinc chloride (81 mg, 0.6 mmol) was heated to reflux with L^1 (50 mg, 0.16 mmol) in methanol (100 cm^3) for 4 h, after which period the solution was evaporated to dryness and dissolved in water (100 cm^3). The aqueous solution was treated with $[NH_4][PF_6]$ (0.2 g) to yield orange-yellow microcrystals of the complex (64 mg, 72%).

$[Ni(L^1)(H_2O)_2][NO_3]_2$. A solution of $Ni(NO_3)_2\cdot 6H_2O$ (100 mg, 0.34 mmol) in methanol (50 cm^3) was treated with L^1 (100 mg, 0.32 mmol) to give a pale brown solution. This was heated to reflux for 3 h, concentrated, and cooled to yield brown crystals of the complex (105 mg, 66%).

$[Mn(L^1)Cl_2]$. This was prepared in the same manner as the nickel complex, using $MnCl_2\cdot 4H_2O$ (70 mg, 0.35 mmol).

$[Cu(L^1)Cl]Cl\cdot 2H_2O$. This was prepared in the same manner as the nickel complex, using $CuCl_2\cdot 2H_2O$ (60 mg, 0.35 mmol). Recrystallization from warm water yielded the blue-green pentahydrate.

Crystal-structure Determination of $[Mn(L^1)Cl_2]$.—A suitable orange-brown block-shaped crystal, obtained by recrystallisation from methanol by slow diffusion of diethyl ether vapour, was mounted on a glass fibre with epoxy resin.

Crystal data. $C_{20}H_{18}Cl_2MnN_4$, $M = 412.20$, orthorhombic, $a = 7.756(1)$, $b = 11.677(1)$, $c = 20.361(2)$ Å, $U = 1\,844.0$ Å^3 (by least-squares refinement on diffractometer angles for 54 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group *Pnab* (alternative *Pbcn*, no. 60), $Z = 4$, $D_c = 1.484$ g cm^{-3}, $F(000) = 900$. Orange-brown blocks. Crystal dimensions (distance to faces from centre): 0.122(001, 001) × 0.061(021) × 0.074(010) × 0.350(100, 100) mm, $\mu(Mo\text{-}K_\alpha) = 9.44$ cm^{-1}.

Table 5. Atomic co-ordinates for [Cu(L^1)Cl]Cl

Atom	*x*	*y*	*z*
Cu(1)	2 000(1)	4 154(1)	996(1)
N(1)	1 312(2)	3 766(8)	245(3)
N(2)	2 290(2)	4 865(9)	450(2)
N(3)	1 720(3)	2 494(11)	1 410(3)
N(4)	2 723(2)	4 298(10)	1 692(3)
C(1)	1 367(3)	4 150(11)	−222(3)
C(2)	825(3)	3 253(11)	185(3)
C(3)	929(3)	4 023(13)	−797(4)
C(4)	366(3)	3 122(12)	−384(4)
C(5)	−148(3)	2 624(14)	−460(4)
C(6)	748(3)	2 871(11)	675(4)
C(7)	434(4)	3 537(12)	−871(4)
C(8)	1 178(3)	3 146(13)	1 300(4)
C(9)	−208(3)	2 255(14)	18(4)
C(10)	1 926(3)	4 619(10)	−105(3)
C(11)	2 051(4)	4 731(12)	−564(4)
C(12)	2 568(4)	5 090(11)	−432(4)
C(13)	2 812(3)	5 278(10)	591(3)
C(14)	3 205(3)	5 591(11)	1 186(3)
C(15)	3 732(3)	5 923(13)	1 309(4)
C(16)	3 889(4)	5 950(14)	875(4)
C(17)	3 063(3)	5 858(13)	1 665(3)
C(18)	3 518(4)	5 702(13)	308(4)
C(19)	2 969(3)	5 370(10)	152(4)
C(20)	236(3)	2 385(13)	573(4)
Cl(1)	1 715(1)	7 578(3)	1 153(1)
Cl(2)	3 525(1)	10 591(4)	2 097(1)
O(1)	2 620(2)	9 210(11)	2 390(3)
O(2)	1 174(3)	8 682(11)	1 939(3)
O(3)	4 719(4)	8 980(16)	2 806(6)
O(4)	256(3)	330(15)	1 853(4)
O(5)	171(8)	−1 872(27)	2 688(9)

Data collection and processing.[15] Stoe-Siemens AED diffractometer, 24-step ω–θ mode with ω scan width = 0.04° for each step, scan time 0.5—2.0 s per step, graphite-monochromated Mo-K_α radiation. 2 876 Reflections measured ($5.0 \leqslant 2\theta \leqslant 45.0°$, $\pm h$, $-k$, $\pm l$), 1 215 unique [merging $R = 0.041$ after numerical absorption correction (maximum, minimum transmission factors = 0.881, 0.793)] giving 959 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Patterson synthesis (Mn and Cl atoms) followed by Fourier difference techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic. Methylene, aromatic, and amino H-atoms in calculated positions with common isotropic thermal parameters for each type. Unit weights gave satisfactory agreement anlyses. Final *R* value was 0.048. Programs and computers used and sources of scattering factor data are given in ref. 15. Final atomic co-ordinates are listed in Table 4.

Crystal-structure Determination of [Cu(L^1)Cl]Cl·5H_2O.—A suitable dark blue-green needle, obtained by recrystallisation from warm water, was mounted on a glass fibre with epoxy resin.

Crystal data. $C_{20}H_{18}Cl_2CuN_4 \cdot 5H_2O$, *M* = 538.91, monoclinic, $a = 28.268(2)$, $b = 7.030(1)$, $c = 26.147(3)$ Å, $\beta = 118.87(1)°$, $U = 4\,550.3$ Å^3 (by least-squares refinement on diffractometer angles for 54 automatically centred reflections $\lambda = 0.710\,69$ Å), space group *C*2/*c* (no. 15), *Z* = 8, $D_c = 1.573$ g cm^{-3}, *F*(000) = 1 992. Dark blue-green needles. Crystal dimensions (distance to faces from centre): 0.095(100, 100) × 0.027(001, 001) × 0.250(010, 010) mm, μ(Mo-K_α) = 11.78 cm^{-1}.

Data collection and processing.[15] As for [Mn(L^1)Cl_2] with scan time 0.75—3.0 s per step and graphite-monochromated Mo-K_α radiation. 7 759 Reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $\pm h$, $-k$, $\pm l$), 4 002 unique [merging $R = 0.047$ after numerical absorption correction (maximum, minimum transmission factors = 0.938, 0.758)] giving 2 759 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Random-start direct methods (Cu and Cl atoms) followed by Fourier difference techniques. Blocked full-matrix least squares with all non-hydrogen atoms except the solvent O atoms anisotropic. Methylene, aromatic, and amino, H-atoms in calculated positions with common isotropic thermal parameters for each type. Several H-atoms from solvent water molecules directly located and refined with O–H distances constrained at 1.10 Å and assigned a common isotropic thermal parameter. The weighting scheme $w = 5.595/[\sigma^2(F) + 0.0005F^2]$ with $\sigma(F)$ from counting statistics gave satisfactory agreement analyses. Final *R* and *R′* values were 0.072 and 0.065. Initial structure solution using SHELX 86,[16] other programs and computers used, and sources of scattering factor data are given in ref. 15. Final atomic co-ordinates are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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