

Studies of Chelates with Heterocyclic Ligands

II. Ionic Nickel(II) and Copper(II) Chelates with 8-Aminoquinoline and some of its Derivatives

PER HALFDAN NIELSEN and OTTO DAHL

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen,
The H. C. Ørsted Institute, Copenhagen, Denmark*

Nickel(II) chelates where 8-aminoquinoline and N,N' -bis-(8-quinolyl)-alkylenediamines function as neutral donors have been investigated. The properties of the N,N' -bis-(8-quinolyl)-tetramethylenediamine chelate with nickel(II) chloride are consistent with the presence of a 7-membered chelate ring. Also, the copper(II) perchlorates of N,N' -bis-(8-quinolyl)-alkylenediamines have been synthesized.

The ultraviolet spectra of the 1:1, 2:1, and 3:1 chelates prepared from 8-aminoquinoline and nickel(II) chloride are tabulated and discussed.

Finally, the range of investigated ligands was extended to include 8-hydrazinoquinoline and some of its derivatives. The stability is apparently much lower for chelates derived from this series.

A study of inner-complexes derived from 8-aminoquinoline (8-AQ) and N,N' -bis-(8-quinolyl)-alkylenediamines has been carried out in this laboratory.¹ This paper describes our results employing the same ligands as neutral donors.

Burrows and Ritchie² have claimed two series of nickel(II) complexes from the mixing of concentrated solutions of 8-AQ in ethanol with nickel(II) salts in water. When equimolar quantities were used bluish-grey chelates were formed with a ligand to metal ratio of 1:1, whilst the use of 2 moles of 8-AQ gave violet 2:1 chelates. This claim, however, could not be substantiated in the present study although using somewhat different conditions complexes with ligand to metal ratios of 1:1, 2:1, and 3:1 have been prepared. Yasuda,³ as a result of measurements of stability constants, has recently reported the existence of the 3:1 complex with nickel(II) in solution, but made no attempt to isolate the crystalline material.

The absorption spectra of the 3:1, 2:1, and 1:1 chelates of 8-AQ and nickel(II) salts in aqueous solution show no unexpected features. The observed

spectra, collated in Table 1, are considered to be due to formation of the ions $[(8\text{-AQ})_3\text{Ni}]^{2+}$, $[(8\text{-AQ})_2(\text{H}_2\text{O})_2\text{Ni}]^{2+}$, and $[(8\text{-AQ})(\text{H}_2\text{O})_4\text{Ni}]^{2+}$, respectively. This is based on (1) the immediate chloride reaction of the solutions and (2) the fact that the spectra are indifferent to either the addition of excess chloride ions or the use of nickel(II) bromide in place of nickel(II) chloride. As the 2:1 chelate crystallises with 2 moles of water, it is reasonable to assume that the same structure is present in the solid phase. To prove this, the infrared spectra of the 3:1 and 2:1 chelates as well as the deuterated compounds were recorded. On comparison, it was observed that in addition to the shifts of the absorptions due to the amino groups on deuteration, only the 2:1 chelate showed a peak at 1030 cm^{-1} (m); this peak was displaced to 892 cm^{-1} (m). This behaviour is characteristic for coordinated water ⁴ and confirms the structure given above for the chelate.

The electronic absorption spectra of the nickel chelate ions had to be studied in 10^{-1} to 10^{-2} M aqueous solutions due to the low stability constants.³ From Table 1 it will be seen that the absorptions arising from the ligand at $40\ 500\text{ cm}^{-1}$ and $29\ 900\text{ cm}^{-1}$ show a hypsochromic shift upon chelation to ca. $43\ 500\text{ cm}^{-1}$ and $33\ 000\text{ cm}^{-1}$. The blue shift of the low frequency ligand absorption has been reported recently,⁵ and attributed to the blocking of the resonance between the amino group and the quinoline ring. We intend to examine this point by extending these studies to include an investigation of the ultraviolet spectra of protonised 8-AQ.

From the frequency range and low intensities observed, and assuming octahedral coordination to be closely approximated, we infer ⁶ that the ligand field absorptions of the nickel(II) chelate ions (Table 1) are due to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transitions. Utsuno and Sone ⁷ have recently discussed the spectra of a series of closely related chelates with the general formulas $[\text{L}_3\text{Ni}]^{2+}$, $[\text{L}_2(\text{H}_2\text{O})_2\text{Ni}]^{2+}$, and $[\text{L}(\text{H}_2\text{O})_4\text{Ni}]^{2+}$, where L = ethylenediamine,

Table 1. Electronic absorption characteristics of 8-AQ and nickel(II) complexes of 8-AQ.*

Solution	Short wave-length bands cm^{-1} (log ϵ)	Long wave-length bands cm^{-1} (log ϵ)	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) cm^{-1} (log ϵ)	${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) cm^{-1} (log ϵ)
8-AQ in H_2O	40 500 (4.41)	29 900 (3.40)		
$[(8\text{-AQ})(\text{H}_2\text{O})_4\text{Ni}]^{2+}$ in H_2O	43 500 (4.53)	31 700 (3.62) 33 100 (3.68) 33 800 (3.67)	16 400 (0.70)	10 500 (0.71)
$[(8\text{-AQ})_2(\text{H}_2\text{O})_2\text{Ni}]^{2+}$ in H_2O	43 300 (4.80)	31 700 (3.94) 33 100 (4.00) 33 800 (3.99)	17 800 (0.93)	11 000 (0.91)
$[(8\text{-AQ})_3\text{Ni}]^{2+}$ in H_2O	43 300 (5.25)	31 700 (4.15) 33 100 (4.20) 33 800sh (4.19)	18 700 (1.01)	11 500 (0.76) 12 700 (0.69)

* In addition to the absorptions given above strong concentration dependent bands were found in the region of $50\ 000\text{ cm}^{-1}$.

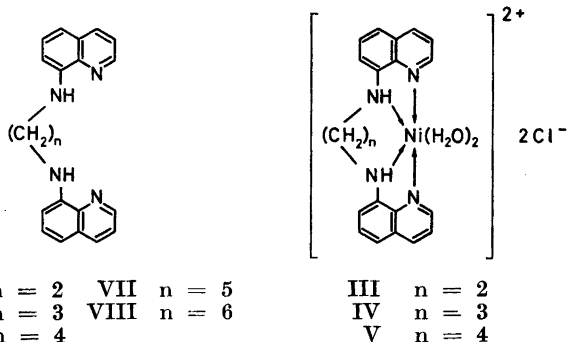
2-picolylamine or 2,2'-dipyridine. Within each of these series, they observed a consistent shift of the absorptions in question towards lower frequencies. The agreement with the results for $L = 8\text{-AQ}$ (Table 1) is satisfactory and supports the validity of the chelate ion structures given.

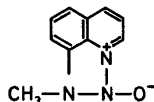
Finally it should be mentioned, that the inner-complexes $(8\text{-AQ})_2\text{Pd}^{8+}$ and $(8\text{-AQ})_2\text{Cu}^{1+}$ as well as 8-AQ in absolute ethanol, have nearly identical ultra-violet spectra. No simple explanation can at present be given for the disagreement with the bathochromic shifts observed for similar chelation of 8-quinolinol.⁹

Chelates of N,N' -bis-(8-quinolyl)-ethylenediamine (I) and -trimethylenediamine (II) with nickel(II) chloride were easily formed in water or ethanol/water mixtures, the diamine functioning as a quadridentate ligand to give the complexes III and IV, respectively. That two moles of crystal water are coordinated to nickel became apparent when the infrared spectra of I–IV were compared with those of the deuterated compounds. The absorptions characteristic of co-ordinated water were found at 970 cm^{-1} (m) in III and 992 cm^{-1} (w) in IV, not far from the one found for the 2:1 8-AQ chelate at 1030 cm^{-1} (m). Therefore, III and IV can be formulated as $[(\text{I})(\text{H}_2\text{O})_2\text{Ni}]\text{Cl}_2$ and $[(\text{II})(\text{H}_2\text{O})_2\text{Ni}]\text{Cl}_2$, respectively.

The corresponding complex V with N,N' -bis-(8-quinolyl)-tetramethylenediamine (VI) as ligand could not be prepared under the same conditions. Instead, VI was dissolved in boiling 1 M NiCl_2 , and from the resulting solution the chelate (V) separated slowly with two moles water, probably coordinated to nickel as in III and IV. As it is rather easily soluble in absolute ethanol and rapidly decomposes in water it is very probably monomeric. Interestingly, an intense red colour was observed for a very short time, when concentrated ice-cold sodium hydroxide was added to the chelate. This is a strong indication¹ that an unstable inner-complex is formed, probably with a seven-membered ring and structurally related to the previous described chelates.

Boiling of N,N' -bis-(8-quinolyl)-pentamethylenediamine (VII) and -hexamethylenediamine (VIII) with a strong aqueous nickel(II) chloride solution caused only very minute amounts to be dissolved. On cooling we isolated from VII a complex with the approximate composition $\text{VII}\cdot 2\text{NiCl}_2$, showing that the ligand behaves as a bifunctional bidentate under these conditions.





X

Formation of ring systems with seven- and higher membered rings has been reported for ionic complexes of alkylenediamines with copper(II) perchlorate,¹⁰ though the possibility of dimeric¹¹ or polymeric structures cannot be excluded. When treating the ligands VI—VIII with copper(II) perchlorate under different conditions, we have made a series of copper chelates which might be analogous in structure to the nickel compounds III—V mentioned above. However, their solubilities suggest a high molecular weight.

8-Hydrazinoquinoline, 8-acetylhydrazinoquinoline, glyoxal-bis-(8-quinolylyl-hydrazone), and a series of 8-quinolylylthiosemicarbazides were all tested for complex formation with nickel(II) chloride. Though some of the chelates formed could be obtained nearly analytically pure, the stability was generally considerable lower than found within the 8-aminoquinoline series. An attempt to make inner-complexes with these ligands by addition of sodium hydroxide, caused complete decomposition within *ca.* 10 min.

In an earlier study,¹ it was proposed that N,N'-bis-nitroso-N,N'-bis-(8-quinolylyl)-ethylenediamine (IX) and 8-quinolinecarbaldoxime have a strong tendency to form mesoionic triazole and diazole rings, respectively. This first assumption has derived further support from the fact that the infrared spectrum of N-nitroso-8-methylaminoquinoline (X) proved quite similar to that of IX. Additional evidence for the structures proposed for 2- and 8-quinolinecarbaldoxime was obtained by comparing their infrared spectra with those of the *O*-methyl derivatives. Apart from the changes expected from the substitution of hydrogen by the methyl group, the spectra of the 2-derivatives were very similar. By contrast, the spectrum of *O*-methyl-8-quinolinecarbaldoxime was much less complicated than that of the parent oxime. Indeed, this latter spectrum not only showed absorptions corresponding to those in the former, but also peaks which could be attributed to the mesoionic structure. As *O*-methylation hinders the tautomerization of the oxime to a diazole structure, these observations support the proposal that 8-quinolinecarbaldoxime, at least in crystalline phase, exists partially in this form.

The ionic, as well as the inner, nickel(II) complexes were treated with nitrogen oxide under various conditions in order to make pentacovalent complexes analogous to those described for the 8-AQ complex with cobalt(II) chloride.¹² All attempts have so far been unsuccessful, infrared spectroscopy showing that, in most cases, decomposition occurred with formation of nitrates.

Finally, we tried to prepare N-oxides of the N,N'-bis-(8-quinolylyl)-alkylenediamines through the Bucherer reaction, using 8-hydroxyquinoline N-oxide instead of 8-hydroxyquinoline. In all instances the only new product isolated was 2,8-dihydroxyquinoline, which is also formed (as acetate) in a rearrangement of the N-oxide with acetic anhydride.¹³

EXPERIMENTAL

The analyses were carried out at the microanalysis department of this laboratory. The absorption spectra were recorded using a Perkin-Elmer model 337 grating infrared spectrophotometer (solid compounds in KBr discs) and a model 137UV ultraviolet-visible spectrophotometer. The range between 10 000 cm^{-1} and 13 333 cm^{-1} was recorded with a Cary model 14 spectrophotometer.

The following amines were prepared by a modified Bucherer reaction according to the directions given for *N,N'*-bis-(8-quinolyl)-ethylenediamine in the previous paper by Jensen and Nielsen.¹

N,N'-Bis-(8-quinolyl)-tetramethylenediamine (VI). Recrystallisation from hexane of the crude product gave pale yellow needles, m.p. 117–118°C, in 48 % yield. The compound is moderately soluble in benzene, but less soluble in ethanol or acetone. (Found: C 76.87; H 6.52; N 16.35. Calc. for $\text{C}_{22}\text{H}_{22}\text{N}_4$: C 77.16; H 6.48; N 16.36).

N,N'-Bis-(8-quinolyl)-2,3-butanediamine. The product obtained from 8-quinolinol and pure *meso*-2,3-butanediamine was recrystallised from hexane to give pale yellow crystals, m.p. 112–113°C, yield 40 %. The apparent homogeneity suggests this to be a pure *meso*-form, thus indicating an interesting synthetic route to optically pure ligands. (Found: C 77.20; H 6.57; N 16.43. Calc. for $\text{C}_{22}\text{H}_{22}\text{N}_4$: C 77.16; H 6.48; N 16.36).

N,N'-Bis-(8-quinolyl)-pentamethylenediamine (VII). This substance was obtained as pale yellow crystals, m.p. 82–83°C, on recrystallisation from cyclohexane, yield 42 %. It is very soluble in benzene and acetone, moderately soluble in cyclohexane and ethanol. (Found: C 77.47; H 6.57; N 15.58. Calc. for $\text{C}_{23}\text{H}_{24}\text{N}_4$: C 77.49; H 6.79; N 15.72).

N,N'-Bis-(8-quinolyl)-1,2-cyclohexanediamine. This compound was prepared using commercial *meso*-1,2-cyclohexanediamine (Fluka pract.) without previous purification. Nearly colourless needles were obtained from hexane, m.p. 137–138°C, yield 36 %. (Found: C 77.95; H 6.49; N 15.40. Calc. for $\text{C}_{24}\text{H}_{24}\text{N}_4$: C 78.23; H 6.57; N 15.21).

Bis-(β -8-quinolylaminoethyl)-amine. 8-Quinolinol and diethylenetriamine gave a 23 % yield of nearly colourless crystals, m.p. 55–7°C, from hexane. The product dissolves easily in benzene to give a yellowish solution. The chemical properties are consistent with the absence of a primary amino group. (Found: C 73.80; H 6.43; N 19.58. Calc. for $\text{C}_{22}\text{H}_{23}\text{N}_5$: C 73.91; H 6.49; N 19.59). The red-brown inner-complex, formed on treatment with nickel(II) chloride and NaOH, could not be obtained analytically pure.

8-Methylaminoquinoline. A slow stream of sulfur dioxide was passed through 1 kg of 33 % aqueous methylamine solution until pH = 6. 70 g 8-quinolinol was added and the mixture refluxed during 3 days. Concentrated sodium hydroxide solution was added until alkaline, and the amine was extracted with chloroform. After being dried over magnesium sulfate and the solvent evaporated, the remaining brown oil was distilled *in vacuo*. The yield was 13 g of a reddish oil, b.p. 96–8°C (3 mm), m.p. 10–11°C. To eliminate the impurities suggested by elemental analysis, the picrate was prepared and recrystallised from absolute ethanol. Long orange-red crystals, m.p. 185–7°C (decomp.). (Found: C 49.70; H 3.58; N 17.97. Calc. for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_7$: C 49.62; H 3.38; N 18.08). The picrate was decomposed with excess aqueous lithium hydroxide. The resultant mixture was then extracted with ether and dried. Evaporation of ether gave a yellowish oil, m.p. 10.5–11°C, from which, however, satisfactory analysis was still not obtained. The reason for this is obscure. (Found: C 75.40; H 6.74. Calc. for $\text{C}_{10}\text{H}_{10}\text{N}_2$: C 75.92; H 6.37).

N-Nitroso-8-methylaminoquinoline. 8-Methylaminoquinoline dissolved in conc. hydrochloric acid was nitrosated with sodium nitrite as described for *N,N'*-bis-(8-quinolyl)-ethylenediamine.¹ The white precipitate formed by adding sodium hydroxide in excess was filtered, washed with water, and dried. Recrystallisation from an ethanol/water mixture gave white needles in 58 % yield, m.p. 99–99.5°C. (Found: C 64.20; H 4.64. Calc. for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}$: C 64.16; H 4.85).

IR-spectrum: 757m, 786s, 795m, 812w, 829m, 856m, 956w, 1031m, 1047s, 1071m, 1130w, 1148m, 1185s, 1207w, 1232s, 1329w, 1384s, 1438s, 1455m, 1475w, 1501m, 1575vw, 1595m, 3020w.

N,N'-Bis-(8-quinolyl)-oxamide. Two moles of 8-aminoquinoline was boiled gently with one mole of diethyl oxalate for 3 h. On cooling and addition of three times the volume of ethanol, a precipitate was formed which was isolated and recrystallised from dioxane to give white needles. M.p. 310.5–311.5°C. (Found: C 69.95; H 4.36; N 16.55. Calc. for $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2$: C 70.16; H 4.12; N 16.37).

8-Hydrazinoquinoline. The dihydrochloride, m.p. 197–199°C (decomp.), was prepared according to Hünig and Werner,¹⁴ but could not be obtained analytically pure. Instead, the hydrazine was liberated with 2 N NaOH, extracted with ether, dried over magnesium sulfate, and the solvent evaporated. The yellow product was recrystallised from cyclohexane to give long colourless needles, m.p. 63.5–64.0°C, which rapidly develop a yellowish tinge in the air. (Lit.¹⁶ gives 64°C). The yield was 80 % based on the dihydrochloride. (Found: C 67.85; H 5.90; N 26.60. Calc. for $C_8H_8N_2$: C 67.90; H 5.70; N 26.40).

8-Acetylhydrazinoquinoline. A dried ether extract of 8-hydrazinoquinoline (crude product) was treated with acetic anhydride and the mixture left for 18 h. The precipitated white needles were collected and washed with ether (yield 59 %). Recrystallisation twice from water, using active carbon, gave a constant m.p. of 154.5–155°C. The compound is extremely soluble in methanol and ethanol. (Found: C 65.90; H 5.64; N 20.66. Calc. for $C_{11}H_{11}N_2O$: C 65.67; H 5.51; N 20.88).

1-(8-Quinolyl)-4-methylthiosemicarbazide. Equimolar quantities of 8-hydrazinoquinoline and methylisothiocyanate in ether gave a white precipitate, which was collected after 24 h and dried. Recrystallisation from ethanol gave 60 % of white crystals, m.p. 196–197°C (decomp.). (Found: C 56.68; H 4.96; S 13.72. Calc. for $C_{11}H_{12}N_2S$: C 56.89; H 5.21; S 13.78).

IR-spectrum: 698m, 759m, 789s, 826m, 881w, 1018w, 1028m, 1047s, 1079w, 1127w, 1172w, 1240m, 1262m, 1315m, 1360m, 1400w, 1438w, 1459w, 1490m, 1505s, 1550s, 1560s sh, 1620w, 2900w, 3220s.

1-(8-Quinolyl)-4,S-dimethylthiosemicarbazide hydroiodide. White crystals were obtained from the above thiosemicarbazide and methyl iodide in benzene. M.p. 157.5–158°C. This salt darkens slowly on standing. (Found: C 38.55; H 4.11. Calc. for $C_{12}H_{15}N_2SI$: C 38.51; H 4.04).

IR-spectrum: 675m br, 714w, 750w sh, 760m, 793m, 827s, 888w, 980w, 1023w, 1050w, 1081w, 1122m, 1162w, 1210w br, 1259w, 1287m, 1323m, 1378m, 1418m, 1472m, 1503s, 1528m, 1580m, 1615vs, 3050s.

The thiosemicarbazides described here are considered to be 1,4-, and not 2,4-derivatives, for the following reasons: (1) reactions expected from a free NH_2 -group cannot be achieved (2) the principal features in the infrared spectra are present in the spectra of related compounds investigated by Jensen and Nielsen.¹⁶

1-(8-Quinolyl)-4-ethylthiosemicarbazide. This product was prepared in the same way as the methyl compound, but using ethylisothiocyanate. The yield was 81 %. Recrystallisation from benzene gave white crystals, m.p. 146.5–148°C. (Found: C 58.85; H 5.73. Calc. for $C_{12}H_{14}N_2S$: C 58.52; H 5.73). The infrared spectrum was very similar to that of the methyl derivative.

1-(8-Quinolyl)-4-propylthiosemicarbazide. The green crude product was obtained in 80 % yield from propylisothiocyanate. Several recrystallisations from benzene, using active aluminium oxide, gave white crystals, m.p. 158–159°C. (Found: C 60.30; H 6.40; N 21.29. Calc. for $C_{13}H_{16}N_2S$: C 59.98; H 6.20; N 21.53). The infrared spectrum proved this to belong to the 1,4-series.

Glyoxal-bis-(8-quinolyl)hydrazone. Equimolar quantities of glyoxal sulphate and 8-hydrazinoquinoline dihydrochloride were dissolved in water and heated $\frac{1}{2}$ h at 50°C. Sodium acetate was added until the red solution turned yellow, and on cooling a yellow brown precipitate was formed. Recrystallisation from cyclohexane gave a 25 % yield of yellow needles, m.p. 165–167°C (decomp.). (Found: C 70.45; H 4.57; N 24.54. Calc. for $C_{20}H_{16}N_6$: C 70.57; H 4.74; N 24.69).

1-(8-Quinolyl)-semicarbazide. In an attempt to prepare β,β' -di-(8-quinolyl)-carbonohydrazide by warming 8-hydrazinoquinoline and urea until a homogeneous melt was formed, we obtained instead the above-mentioned semicarbazide. On recrystallisation of the crude greenish product from dimethylformamide, white crystals were obtained, m.p. 233°C. (Lit.¹⁵ gives 235°C). (Found: N 27.86. Calc. for $C_{16}H_{10}N_4O$: N 27.71). When this substance was heated further with 8-hydrazinoquinoline, only very small quantities of somewhat impure β,β' -di-(8-quinolyl)-carbonohydrazide could be isolated with m.p. 251–254°C (decomp.) after recrystallisation from ethanol. (Found: C 66.05; H 5.22. Calc. for $C_{19}H_{14}N_6O$: C 66.26; H 4.68).

2-Quinolincarbaldehyde dinitrophenylhydrazone. This product was prepared, in the usual way, as yellow crystals, m.p. 244–246°C after recrystallisation from ethanol. (Found: C 57.17; H 3.63; N 20.67. Calc. for $C_{16}H_{11}N_5O_4$: C 56.97; H 3.29; N 20.77). We

have previously reported,¹ that the mononitrophenylhydrazone forms violet coloured solutions with nickel(II) chloride and alkali. This cannot, however, be taken to indicate complex formation as proposed, since the same colour is formed without the addition of nickel(II) ions. On the contrary, it seems to be due to the formation of an *aci*-nitro form, since the dinitrophenylhydrazone gives a red colour in the same way with dilute sodium hydroxide.

O-Methyl-2-quinolinecarbaldoxime. This substance was prepared from 2-quinoline-carbaldehyde and methoxyammonium chloride and recrystallised from hexane to give white crystals, m.p. 50.5–51.5°C. (Found: N 15.26. Calc. for C₁₁H₁₀N₂O: N 15.05).

IR-spectrum: 749m, 760m sh, 789w, 831m, 897w, 922m, 935m, 1051vs, 1112w, 1138w, 1179w, 1204w, 1298w, 1345w, 1373w, 1425m, 1455w, 1501m, 1552w, 1594m, 1611w, 2925m, 3020w.

O-Methyl-8-quinolinecarbaldoxime. The crude product obtained from 8-quinoline-carbaldehyde and methoxyammonium chloride was recrystallised twice from hexane and once from an ethyl acetate/hexane mixture to give white crystals, m.p. 53.5–54.5°C. (Found: N 15.25. Calc. for C₁₁H₁₀N₂O: N 15.05).

IR-spectrum: 752m, 764m, 791s, 807w, 827m, 881m, 916s, 944w, 1022s, 1033s, 1055vs, 1085m, 1130w, 1163w, 1247w, 1306w, 1324w, 1360w, 1387w, 1422w, 1439w, 1462w, 1494m, 1566m, 1580m, 1607w, 2880w, 2920w, 2980w.

1,2,3,4-Tetrahydro-7-propyl-8-quinolinol. This substance was isolated as a by-product on hydrogenation of 7-allyl-8-quinolinol with hydrogen and Raney-nickel in ethanol. Long white needles from ethanol, m.p. 73.5–74.5°C. It dissolves easily in dilute aqueous sodium hydroxide showing that hydrogenation of the pyridine ring has been accomplished. This is confirmed by the appearance of an NH stretching vibration in the IR-spectrum at 3300 cm⁻¹ when compared to 7-propyl-8-quinolinol. (Found: C 75.05; H 8.92; N 7.45. Calc. for C₁₂H₁₇NO: C 75.35; H 8.96; N 7.32).

The metal chelate compounds. The usual method for making these compounds, *i.e.* mixing equivalent quantities of the ligand dissolved in ethanol with an aqueous solution of the metal salt, gave, in many instances, unsatisfactory analyses. Furthermore, the ionic complex compounds are often extremely soluble in the water-ethanol mixtures formed. Much better results were, in general, obtained when the finely pulverised ligand was boiled for some time with an aqueous solution of the metal salt until a clear solution was obtained. The metal chelate then precipitates analytically pure on cooling the resulting, filtered and occasionally somewhat concentrated, solution.

8-Quinolylaminenickel(II) chloride monohydrate. The ligand (0.131 g) in 3 ml acetone and nickel(II) chloride hexahydrate (0.127 g) in 4 ml ethanol (equimolar quantities) were mixed to give a clear green solution from which the chelate settled within a few minutes. An 88% yield of pale grey-olive crystals was obtained after the product was washed with absolute ethanol and dried $\frac{1}{2}$ h at 25°C and 10 mm Hg. On heating decomposition occurred between 210 and 270°C. (Found: C 37.32; H 3.53; Cl 24.57; N 9.74; Ni 20.16. Calc. for C₉H₁₀Cl₂N₂NiO: C 37.04; H 3.46; Cl 24.30; N 9.60; Ni 20.12).

The chelate is nearly insoluble in ethanol. When dissolved in water decomposition occurs to nickel(II) chloride and 2:1 chelate.

Bis-(8-quinolylamine)-nickel(II) chloride dihydrate. 8-Aminoquinoline (1.44 g) and nickel(II) chloride hexahydrate (1.19 g) were dissolved in 150 ml of 96% ethanol and left in a refrigerator overnight. The grey-green precipitate was collected and dried as above. Yield 55%. The substance decomposes on heating at 220–250°C. The solubility is moderate in water and ethanol. (Found: C 47.32; H 4.42; Cl 15.28; N 12.46; Ni 12.97. Calc. for C₁₈H₂₀Cl₂N₄NiO₂: C 47.63; H 4.44; Cl 15.63; N 12.34; Ni 12.93).

Tris-(8-quinolylamine)-nickel(II) chloride monohydrate. 8-Aminoquinoline (0.412 g) and nickel(II) chloride hexahydrate (0.238 g) were boiled for a short time with 10 ml water. The red solution was filtered, concentrated to 2 ml, and allowed to stand for 2 h at 5°C. The precipitated pale yellow-brown complex was washed with a little water and dried *in vacuo* over KOH. The yield was variable, generally around 50%. The complex decomposes on heating at 260–270°C. (Found: C 55.52; H 4.65; Cl 12.42; N 14.75; Ni 10.30. Calc. for C₂₇H₂₈Cl₂N₆NiO: C 55.90; H 4.52; Cl 12.22; N 14.49; Ni 10.12).

[N,N'-Bis-(8-quinolyl)-ethylenediamine]nickel(II) chloride dihydrate. A solution of nickel(II) chloride hexahydrate (2.38 g) in 40 ml water was boiled with the ligand (3.14 g) for *ca.* 15 min. A clear blue-violet solution was formed. The crystals precipitated after 24 h were collected, washed with very little water and dried *in vacuo*. The yield of

pale greenish-blue crystals, which decompose without melting at 260–270°C, was 60 %. (Found: C 49.68; H 4.87; Cl 14.70; N 11.63; Ni 12.02. Calc. for $C_{20}H_{22}Cl_2N_4NiO_2$: C 50.05; H 4.62; Cl 14.77; N 11.67; Ni 12.23).

[*N,N'*-Bis-(8-quinolyl)-trimethylenediamine]nickel(II) chloride dihydrate. This chelate was prepared as above but it proved necessary to evaporate the lilac solution to obtain a precipitate. The yield, of sea-green crystals with m.p. 235–240°C after some decomposition, was 58 %. (Found: C 50.92; H 4.95; Cl 14.61; N 11.54; Ni 12.10. Calc. for $C_{21}H_{24}Cl_2N_4NiO_2$: C 51.06; H 4.90; Cl 14.36; N 11.35; Ni 11.89).

[*N,N'*-Bis-(8-quinolyl)-tetramethylenediamine]nickel(II) chloride dihydrate. The ligand was boiled for 1 h with 1 M aqueous nickel(II) chloride. The filtered solution was kept at 5°C overnight and the green-blue needles (or ultramarine-grey microcrystals) were isolated and washed with absolute ethanol. The yield was 61 % after drying $\frac{1}{2}$ h at 25°C and 10 mm Hg. (Found: Cl 13.94; N 10.88; Ni 11.48. Calc. for $C_{22}H_{26}Cl_2N_4NiO_2$: Cl 13.96; N 11.03; Ni 11.56). After being dried 1 h at 100°C, the crystals turned pale green. The anhydrous complex absorbs water immediately when exposed to air. (Found: Cl 15.20; N 11.75; Ni 12.48. Calc. for $C_{22}H_{26}Cl_2N_4Ni$: Cl 15.03; N 11.87; Ni 12.44). On stronger heating the complex decomposes at 215–220°C. When treated with water, immediate decomposition occurs yielding the ligand and nickel(II) chloride.

The analytical values obtained for the copper(II) perchlorate complexes described below are not entirely satisfactory. The reason for this is that they deflagrate violently when submitted to combustion.

[*N,N'*-Bis-(8-quinolyl)-ethylenediamine]copper(II) perchlorate. Copper(II) perchlorate hexahydrate (0.13 g) in 2 ml absolute ethanol was mixed with a solution of *N,N'*-bis-(8-quinolyl)-ethylenediamine (0.102 g) in 20 ml hot absolute ethanol. The blue precipitate, after being washed twice with absolute ethanol and then dried $\frac{1}{2}$ h at 25°C and 10 mm Hg, gave 83 % of blue-green complex. When heated, decomposition occurred at 220–225°C without melting. (Found: C 42.00; H 3.47; Cl 12.55; N 9.60. Calc. for $C_{20}H_{18}Cl_2CuN_4O_8$: C 41.65; H 3.14; Cl 12.30; N 9.71). The prussian-blue monohydrate was obtained in the same way from an ethanol/water mixture. (Found: Cl 11.77; N 9.30. Calc. for $C_{20}H_{20}Cl_2CuN_4O_5$: Cl 11.91; N 9.42).

[*N,N'*-Bis-(8-quinolyl)-trimethylenediamine]copper(II) perchlorate. Preparation as above from ethanol or ethanol/water mixtures gave the prussian-blue complex, which decomposes on heating at 245–250°C. Attempted recrystallisation from water resulted in partial decomposition. (Found: C 42.52; H 3.76; Cl 11.97; N 9.38. Calc. for $C_{21}H_{20}Cl_2CuN_4O_8$: C 42.69; H 3.41; Cl 12.00; N 9.48).

[*N,N'*-Bis-(8-quinolyl)-tetramethylenediamine]copper(II) perchlorate. The olive-grey complex was prepared as above from an ethanol/water mixture except that it was found necessary to concentrate the solution and allow it to stand in a refrigerator overnight. Like the following, but in contrast to the above-mentioned copper(II) perchlorate complexes, this compound is insoluble in water and ethanol and decomposes rapidly in boiling water. On heating decomposition occurs at 190–195°C. (Found: C 43.12; H 3.38; Cl 11.84; N 8.96. Calc. for $C_{22}H_{22}Cl_2CuN_4O_8$: C 43.69; H 3.67; Cl 11.72; N 9.26).

[*N,N'*-Bis-(8-quinolyl)-pentamethylenediamine]copper(II) perchlorate dihydrate. Preparation in absolute ethanol as above gave a pale violet-grey complex in 70 % yield. The complex decomposes at 215–220°C. (Found: C 42.62; H 4.51; N 8.49. Calc. for $C_{23}H_{28}Cl_2CuN_4O_{10}$: C 42.18; H 4.31; N 8.56).

[*N,N'*-Bis-(8-quinolyl)-hexamethylenediamine]copper(II) perchlorate trihydrate. The blue-green complex was obtained in nearly quantitative yield by mixing equimolar quantities of the ligand in ethanol and copper(II) perchlorate in water. This complex decomposes at 170–175°C. (Found: C 41.18; H 4.52; Cl 10.13; N 8.14. Calc. for $C_{24}H_{32}Cl_2CuN_4O_{11}$: C 41.97; H 4.70; Cl 10.32; N 8.16).

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