

Studies of Chelates with Heterocyclic Ligands

I. Chelates Derived from *N,N'*-Bis-(8-quinolyl)-ethylenediamine and Analogous Compounds

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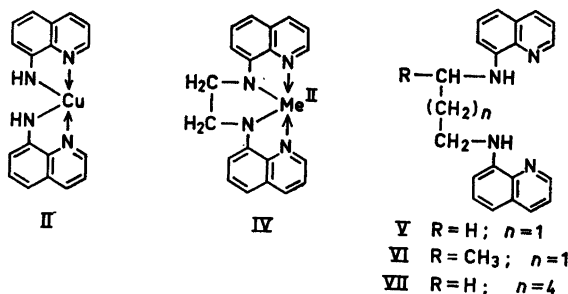
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In strongly alkaline solution 8-quinolylderivatives of ethylenediamine, propylenediamine and 1,3-butanediamine form inner-complex compounds in which they function as anionic, quadridentate ligands. The infrared spectra of the inner-complexes show characteristic differences from the spectra of the parent compounds. The spectra are discussed in detail and an attempt is made to explain the shifts.

The complex-forming properties of several other derivatives of 8-aminoquinoline and some derivatives of 2-quinolinecarbaldehyde were tested qualitatively.

On nitrosation *N,N'*-bis-(8-quinolyl)-ethylenediamine forms a compound which has the composition of a dinitroso compound but does not chemically behave as such. On the basis of its infrared spectrum this compound is formulated as a mesoionic triazole derivative (XIV). A comparison of the infrared spectra of the oximes of 2-quinolinecarbaldehyde and 8-quinolinecarbaldehyde points to the presence of a similar mesoionic ring system in 8-quinolinecarbaldoxime.

Investigations into the chelating properties of 8-aminoquinoline (I) and its derivatives have been rather neglected. Some compounds are known in which the free amine enters as a neutral ligand,^{1,2} but the amine may also function as a weak acid forming inner-complex compounds analogous to the 8-quinolinolates. These are formed in strongly alkaline solution and are easily hydrolysed. The copper compound (II) is obtained as a red-brown powder with the correct composition on recrystallisation from toluene, but the corresponding nickel compound (green) and cobalt compound (red) could not be obtained analytically pure and their infrared spectra show that they contain hydroxides and free 8-aminoquinoline, *i.e.* that some hydrolysis has taken place. We have found that more stable chelates can be formed from *N,N'*-bis-(8-quinolyl)-ethylenediamine (III), which may form a divalent anion functioning as a quadridentate ligand (IV).



The preparation of N,N'-bis-(8-quinolyl)-ethylenediamine from 8-aminoquinoline and ethylene chloride or from 8-bromoquinoline and ethylenediamine has been claimed in a patent.³ No melting point or other physical properties were given and several attempts to repeat the preparation according to the directions failed completely. However, it was found that this compound could be prepared in satisfactory yield by a modified Bucherer-reaction from 8-hydroxyquinoline and ethylenediamine. The homologues derived from trimethylenediamine (V), 1,3-butanediamine (VI), and hexamethylenediamine (VII) were prepared in the same way. From *o*-phenylenediamine only the N-mono-8-quinolylderivative (VIII) could be obtained.

Alcoholic solutions of the bis-(8-quinolyl)-diamines III, V, and VI are coloured dark green on addition of a solution of copper(II) chloride. On addition of NaOH the first solution gives a violet precipitate whilst the other two give a red precipitate, soluble in benzene with a red-violet colour. Cobalt(II) chloride gives with III a red solution, (turning violet on standing in air because of oxidation), which on addition of NaOH gives a red-violet precipitate. With nickel(II) there is no indication of complex-formation in neutral solution, but on addition of NaOH a violet precipitate is formed. Since it proved difficult to purify the copper and cobalt complexes we have especially studied the nickel compounds in detail. These are very soluble in various organic solvents giving a dark blue, dark green or violet solution, depending on the solvent.

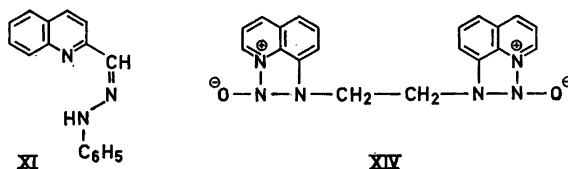
When the hexamethylene derivative (VII) was tested in the same way, only the metal hydroxides were obtained on addition of sodium hydroxide. (With copper(II) chloride a transient red colour was observed). Consequently no stable chelates are formed in accordance with the assumption that the distance between the two quinolyl groups is so great as to prevent the compound from functioning as a quadridentate ligand.

N-(8-Quinolyl)-*o*-phenylenediamine (VIII) gives with nickel(II) chloride and sodium hydroxide a violet precipitate which is only slightly soluble in the common organic solvents and therefore seems to be of a different type of complex (possibly a polymer).

That the nickel chelates are derived from the anions of the compounds III, V, and VI is clearly indicated by the absence of the N—H stretching vibration in the infrared spectra of the chelates. The infrared spectra show some interesting features which will be discussed below.

We have further prepared the hitherto unknown di-(8-quinoly)-amine, $(C_6H_9N)_2NH$ (IX). This amine gives a very characteristic reaction with nickel salts: On addition of nickel(II) chloride a red solution is formed which on addition of sodium hydroxide gives a flaming red precipitate. This amine probably functions as a terdentate ligand, but it has not been possible to isolate the compound in a well defined form.

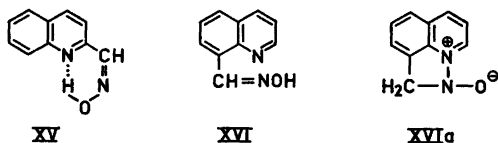
Acylated 8-aminoquinolines show less tendency to form inner-complexes than quinoline-8-aminoquinoline itself. Copper(II) salts were formed from 8-acetamidoquinoline (green), 8-benzamidoquinoline (brown) and 8-*p*-toluenesulfonamidoquinoline (brown). According to Gall and Erlenmeyer,⁴ 8-trichloroacetamidoquinoline gives a violet copper complex. However, these compounds are unstable in the presence of excess sodium hydroxide or ammonia, whilst no nickel or cobalt complexes could be prepared. *N,N'*-Bis-(8-quinolinesulfonyl)ethylene-diamine (X) did not give a colour reaction even with copper(II) salts. This is in accordance with the fact that the increased acid strength of amides in comparison with amines is caused by a resonance effect which diminishes the electron density of the nitrogen atom; it is well known that amides are usually bad complexing agents and when they do form complexes the metal atom is bound to the oxygen atom. It would be of interest to try the effect of a substituent which increases the acid strength of the amino group by a purely inductive effect, *e.g.* the trichloromethyl group. However, an attempt to prepare this compound failed and thus this type of effect was not further explored. The effect of increasing the acid strength of an NH-group was, however, demonstrated qualitatively by the behaviour of the phenylhydrazone (XI) and *p*-nitrophenylhydrazone (XII) of quinoline-2-carbaldehyde, as (XI) does not show any tendency to form chelates in alkaline solution, whilst (XII) with copper(II) salts or nickel(II) salts gave a violet solution on the addition of sodium hydroxide. Quinoline-2-carbaldehyde thiosemicarbazone (XIII) gave a strong yellow colour with the same metal salts; this colour was stable to the addition of sodium hydroxide, indicating that inner-complex compounds had already been formed in neutral solution.



In connection with these studies we also prepared the dinitrosoderivative of III with the intention of reducing it to the corresponding hydrazine. Unexpectedly it was found to be extremely resistant to reduction. This is very unusual, and can probably be explained best by assuming that the nitroso groups have reacted with the quinoline rings to form two mesoionic triazole rings (XIV). This assumption is borne out from consideration of the infrared spectrum of the supposed nitroso compound. In this the pattern of the infrared spectrum of the parent amine has been thoroughly changed: the strong bands at 1522 cm^{-1} and 1576 cm^{-1} , due to the quinoline ring, have disappeared, and no new

bands in the 1300–1600 cm^{-1} range, which could be attributed to a nitrosamine structure, have appeared.

On the basis of this observation it was also thought that 8-quinolinecarbaldoxime might have a similar ring structure, and in fact a comparison of the infrared spectra of the oximes of 2-quinolinecarbaldehyde (XV) and 8-quinolinecarbaldehyde (XVI) lent some support to this assumption. None of these compounds have any infrared bands in the 1640–1680 cm^{-1} region which seems to exclude a normal oxime structure. The spectrum of (XV) has broad bands in the 2700–2900 cm^{-1} region — an indication of strong intramolecular hydrogen bonds. On treatment of (XV) with heavy water these bands are weakened and two new bands appear in the 2000–2500 cm^{-1} range, whereas the spectrum below 2000 cm^{-1} is practically unchanged. This indicates that only the hydrogen atom of the OH group is exchanged on deuteration and points to structure (XV) with intramolecular chelation through the hydrogen atom. The infrared spectrum of XVI shows no indication of hydrogen bonds and the bands near 1570 and 1600 cm^{-1} found in the spectra of all other quinoline derivatives mentioned here, except the "nitroso" compound (XIV), are only weak. On deuteration a radical change of the spectrum takes place indicating that not only oxygen-bound but also carbon-bound hydrogen is being replaced by deuterium. These facts might be explained by assuming that 8-quinolinecarbaldoxime in the solid state has the structure (XVIa) but easily tautomerizes to (XVI). Chemically this compound behaves as an oxime and it should also be noted that both XV and XVI show the same chelating properties towards ions of the transition metals.



DISCUSSION OF THE INFRARED SPECTRA

The infrared spectra of the compounds I, III, V, and VI and their copper(II) or nickel(II) inner-complexes have been summarised in Table 1.

Apart from the disappearance of the N—H stretching band, when the compounds III, V, and VI form inner-complexes, the infrared spectra of the amines and their chelates show the same over-all pattern. However, the formation of metal chelate bonds seems to be responsible for small, but important shifts of frequencies.

The 1460–1625 cm^{-1} region. In this region all the compounds have four strong bands, which are due to the C=C and C=N vibrations of the aromatic ring-system. In addition, 8-aminoquinoline shows a strong band at 1619 cm^{-1} which would be expected from the NH_2 deformation. Deuteration of 8-aminoquinoline shows clearly that not only this band, but also the one at 1602 cm^{-1} can be accounted for to a great extent, by the N—H deformation mode, probably coupled with a ring stretching mode. The persistence of a doublet at

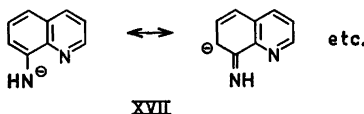
Table 1. Infrared bands of 8-aminoquinoline derivatives [cm⁻¹].

I	II	III	IV	V	Va	VI	VIa	
639 w 704 w	639 w	639 w		642 w	629 w	639 vw		N-H
	732 s 744 m		722 m 726 m		723 m 729 m		716 m 723 m	
754 m 762 m		751 m		738 vs 757 w		743 m 751 m	762 m 771 m	
792 s	784 s	790 vs	776 m	792 s	774 s	794 s		
	803 m		805 m		802 m 807 m		801 m	
821 s	814 m	811 m 817 m 824 m	820 w	819 s	822 w	819 m		
	829 w 1039 w 1073 m	1079 vw	1073 w 1094 w	1096 w	1092 m	1078 vw 1099 w	1049 vw 1106 vw 1121 w	
1097 w 1127 w	1108 s 1139 w 1165 m 1204 m	1129 m 1139 w	1137 m 1145 m 1188 m	1118 m 1131 m	1154 s 1184 w 1199 m 1216 w	1132 w 1142 m 1162 m	1133 vw 1157 m 1190 w	
			1210 m		1224 w 1235 w 1269 w	1224 vw 1237 w	1219 w	
	1233 m 1250 w 1293 w	1234 w 1271 w		1237 m 1277 vw 1292 vw			1292 vw	
		1304 w			1302 w		1318 vw	
1339 m		1344 m	1325 m	1340 s		1341 m		C-N
1374 s 1398 vw	1354 s 1383 vs	1384 vs	1352 m 1380 m 1392 s 1408 vs	1383 vs	1345 s 1384 vs 1401 vs	1381 vs	1343 s 1381 vs 1397 s	C-N
1431 w	1407 w 1434 m	1429 m 1449 w	1450 m 1472 m	1427 m 1449 w 1473 vs 1482 s	1429 w 1449 m 1474 s	1429 m 1457 m	1426 w 1446 w 1471 s	CH ₂
1474 m	1469 vs	1479 vs				1480 s		
1508 s	1504 vs	1522 vs	1502 vs	1520 vs	1504 vs	1519 vs	1502 vs	aromat.
1570 m	1566 vs	1576 s	1565 vs	1575 vs	1565 vs	1576 vs	1561 vs	C=C and C=N
1602 m 1619 s	1586 m 1597 s	1612 m	1586 s	1611 m	1591 s	1610 m	1588 m	
		2850 w 2880 w	2800 m 2920 m	2870 w 2945 w	2680 w 2815 m 2930 m	2865 m 2945 vw 2970 vw	2675 vw 2805 w 2920 w 2960 w 3060 w	N-H aliphatic C-H
3020 m	3045 m	3040 vw	3040 m	3040 w	3060 m	3060 vw		arom. C-H
3340 s 3470 s	3370 s	3370 m		3380 m		3390 m		N-H

- I = 8-Aminoquinoline (II = Cu-chelate).
 III = Bis-N,N'-(8-quinolyl)-ethylenediamine. (IV = Ni-chelate).
 V = Bis-N,N'-(8-quinolyl)-trimethylenediamine. (Va = Ni-chelate).
 VI = Bis-N,N'-(8-quinolyl)-1,3-butanediamine. (VIa = Ni-chelate).

1586 cm^{-1} and 1597 cm^{-1} in the spectrum of the copper salt (II) can not at present be explained; deuteration studies are useless here, as II is prone to hydrolysis on deuteration with D_2O . Deuteration of III showed no weakening of the bands in this region, so the assignment of these as being due to ring vibrations is justified.

It is noteworthy that there is a consistent shift to lower frequencies when the spectrum of the parent compound is compared with that of the corresponding inner-complex. We presume that the explanation of this phenomenon should be sought in the fact that a negative charge on the nitrogen atom will increase the double bond character of the C—N bond and accordingly diminish the double-bond character of the aromatic bonds (XVII). The shifts are small for 8-aminoquinoline but amount to 10–20 cm^{-1} for the compounds III,



V, and VI, and so there can be little doubt that they are real. Since the inner-complexes of these compounds are soluble in chloroform their infrared spectra were also compared with the spectra of the parent compounds in solution and the same shifts were found as for the solid compounds.

When 8-aminoquinoline functions as a neutral ligand as in the compounds $\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ¹ its infrared spectrum is unchanged in this region within the experimental error.

The 1330–1400 cm^{-1} region. All the compounds have a medium to strong band near 1340 cm^{-1} which is probably a C—N stretching band. In accordance herewith it is shifted to higher frequencies when the amine is transformed into an anionic ligand (*cf.* XVII), *i.e.* a shift in the opposite direction to that discussed above.

It may be significant that in the spectrum of $\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ this band is shifted to a lower frequency (from 1339 cm^{-1} to 1318 cm^{-1}). At any rate this is what would be expected, because the lonepair of the NH_2 group is engaged when 8-aminoquinoline functions as a neutral ligand and accordingly, the double-bond character of the C— NH_2 bond should be diminished.

In addition to this band all the compounds listed in Table 1 show a strong peak near 1380 cm^{-1} . This is also found in the spectra of other 8-aminoquinoline derivatives, such as N-(8-quinolyl)-*o*-phenylenediamine (1376 vs) and 8-acetamidoquinoline (1385 vs), and also in the spectra of some other quinoline derivatives, *e.g.* 8-quinolinecarboxylic acid (1385 s). It therefore seems to be due to a vibration of the quinoline ring system. It is not changed in a systematic way when the amines are transformed into the complexes. However, when the compounds III, V, and VI (but not I) are transformed into inner-complexes one or two new strong bands appear at slightly higher frequencies. They may be due to the weak CH_2 —N vibration which is reinforced when the nitrogen atom assumes a negative charge.

The 1100–1160 cm^{-1} region. The two peaks in this region of the spectra of the compounds I and III appear to be at least partly due to an NH vibrational

mode since they are shifted on deuteration. On the contrary, the spectrum of the copper compound II exhibits only one strong band at 1108 cm^{-1} , which is probably analogous to a band in the same place in the spectra of 8-quinolinolates and is very characteristic of these, since its position is dependent on the stability constant.⁵ A corresponding band is not found in the spectra of 8-aminoquinoline or 8-quinolinol, nor in the spectra of the compounds III, V, and VI or their chelates. We suggest that this vibration is a C—H deformation mode which is sensitive to the formal charge on the nitrogen or oxygen atom. Its absence in the spectra of the chelates of compounds III, V, and VI could then be explained by the more rigid structure of the quadridentate ligands. An alternative explanation could be found if one considers the difference between the structure of the inner-complex II and those of compounds IV, Va, and VIa to be due to the ring nitrogen, being situated in the *trans*-position in the former but necessarily in the *cis*-position for the latter compounds.

The 700–1000 cm⁻¹ region. In this region there are some remarkable differences in the spectra of the amines and their innercomplexes. A strong band at $790\text{--}794\text{ cm}^{-1}$ in the spectra of the compounds I, III, V, and VI probably corresponds to the strong 780 cm^{-1} band of 8-quinolinol. According to Bellamy⁶ this is due to a C—H out-of-plane deformation mode. The same may be true of one or two other strong to medium strong bands near 750 cm^{-1} . These bands are shifted to higher frequencies in the spectra of the complexes, which is as expected, since the strength of the C—H bonds will be increased when the NH group is dissociated so that the nitrogen atom acquires a negative charge.

The weak band at 704 cm^{-1} in the spectrum of 8-aminoquinoline is shown by deuteration to be at least partly due to an NH vibrational mode.

EXPERIMENTAL

The analyses were done at the microanalyses department (chief-analyst: Mr. P. Hansen) of this laboratory. The infrared spectra of the solid compounds in KBr were recorded on a Perkin-Elmer model 21 spectrophotometer with NaCl optics.

8-Aminoquinoline (I) was prepared by the reduction of 8-nitroquinoline with iron powder in acetic acid, or more conveniently by a Skraup synthesis from *o*-nitroaniline followed by reduction of the crude 8-nitroquinoline product.⁷ The latter method can be considered reliable for laboratory preparations (yield 50 %). When further purification was needed, the product was steam-distilled.

Di-8-quinolyamine (IX). A suspension of 8-aminoquinoline (14.2 g), sodium pyrosulfite (60 g) and an excess of 8-quinolinol (45 g) in 250 ml water was refluxed gently for one week. The mixture was cooled, treated with 2 N NaOH, and the remaining solid collected on a filter and washed with water until neutral. Excess 8-aminoquinoline was removed by steam distillation and the remaining solid purified by recrystallisation from benzene/ethanol mixture followed by hexane or heptane. The yield was 16 % of long yellowish needles, which slowly darkened in the air; m.p. $132.7\text{--}133.4^\circ\text{C}$. (Found: C 79.75; H 4.70; N 15.42. Calc. for $\text{C}_{18}\text{H}_{13}\text{N}_3$: C 79.68; H 4.83; N 15.49). The compound is easily soluble in benzene, but somewhat less soluble in ethanol.

When an ethanolic solution is treated with NiCl_2 followed by NaOH a dark red precipitate is formed, but this has a non-stoichiometric composition.

IR-spectrum: 714 m, 729 s, 735 s, 745 w, 788 s, 801 m, 815 m, 859 w, 1104 m, 1170 m, 1232 w, 1270 vw, 1329 s, 1388 vs, 1423 m, 1451 w, 1485 s, 1501 m, 1530 vs, 1566 vs, 1591 w, 1611 vw, 3060 w, 3290 w.

N,N'-Bis-(8-quinolyl)-ethylenediamine (III). This compound could not be prepared according to the directions given in the literature³ but was obtained by a modified Bucherer-reaction: a mixture of 8-quinolinol (290 g), ethylene diamine monohydrate (78 g), sodium pyrosulfite (380 g) and water (2 l) was refluxed and mechanically stirred for one week. The solution was made strongly alkaline, cooled and filtered. The solid product was extracted several times with hot 0.2 N NaOH until the removal of sodium 8-quinolinolate was complete, dried and crystallised from acetone (smaller portions preferably from ethanol). Yield 50 g (16 %) of yellowish plates with m.p. 158°C. (Found: C 76.25; H 5.69; N 17.90. Calc. for $C_{30}H_{18}N_4$: C 76.40; H 5.77; N 17.82).

In the same way the following compounds were prepared:

N,N'-Bis-(8-quinolyl)-trimethylenediamine (V). This compound was obtained as light yellow plates after recrystallisation from ethanol, m.p. 105–106°C, yield 47 %; It was insoluble in light petroleum, but easily soluble in benzene. (Found: C 76.50; H 6.13 N 17.04. Calc. for $C_{31}H_{20}N_4$: C 76.80; H 6.14; N 17.06).

N,N'-Bis-(8-quinolyl)-butane-1,3-diamine (VI). The crude product was washed with ethanol to remove the oily contaminants to give 38 % yield of the crystalline compound. This was recrystallised from ethanol or benzene/ethanol mixture (1:3) to give light yellow plates, with a m.p. of 118.5–119.5°C. It was easily soluble in benzene, but less soluble in ethanol and acetone. (Found: C 77.25; H 6.35; N 16.45. Calc. for $C_{22}H_{22}N_4$: C 77.16; H 6.48; N 16.36).

N,N'-Bis-(8-quinolyl)-hexamethylenediamine (VII). The yield of the crude crystalline product was 41 %. From hexane it crystallised as light yellow needles, whilst from ethanol or ethanol/benzene mixture one obtained plates; m.p. 95–96°C. (Found: C 77.55; H 6.96; N 15.02. Calc. for $C_{24}H_{26}N_4$: C 77.80; H 7.07; N 15.12). It had no chelating properties.

IR-spectrum: 639 vw, 724 w, 750 m, 756 w, 792 m, 800 vw, sh, 815 m, 1080 vw, 1096 vw, 1128 w, 1143 w, 1166 vw, 1235 w, 1273 vw, 1305 vw, 1335 m, 1378 vs, 1427 m, 1448 w, 1470 m, 1480 m, 1518 vs, 1575 s, 1609 m, 2865 m, 2940 m, 3050 w, 3070 w, 3400 s.

N-(8-Quinolyl)-*o*-phenylenediamine (VIII). In this case a crystal of iodine was added to the preparative mixture. Recrystallisation from ethanol gave 6–11 % yield of golden-yellow crystals; m.p. 115–115.5°C. (Found: N 17.85. Calc. for $C_{15}H_{13}N_3$: N 17.86). Experiments with a four-fold excess of 8-quinolinol failed to give the diquinolylic compound. The inner-complexes with copper(II) (black) and nickel(II) (red violet) were not investigated further.

IR-spectrum: 635 vw, 712 vw, 755 s, 788 m, 819 m, 902 vw, 1065 vw, 1089 w, 1131 w, 1154 vw, 1171 w, 1241 m, 1260 w, 1271 vw, 1302 m, 1331 m, 1373 s, 1420 w, 1432 vw, 1460 m, 1477 m, 1501 vs, 1512 vs, 1571 m, 1585 w, 1611 s, 3060 vw, 3200 vw, 3325 s, 3460 m.

The metal chelate compounds. An ethanolic solution of the ligand was mixed with an aqueous solution of the metal salt. The chelate formed was converted into the corresponding inner-complex by treatment with an excess of 2 N NaOH; the precipitate could conveniently be isolated by means of filtration on a sintered glass funnel.

Bis-(8-quinolineamino)-copper(II). Recrystallisation from toluene furnished a red-brown crystalline compound; m.p. 205°C with decomp. (Found: C 61.79; H 4.04; N 16.02. Calc. for $C_{18}H_{14}N_4Cu$: C 61.95; H 4.18; N 15.89). The corresponding nickel(II) compound could not be obtained analytically pure.

N,N'-Bis-(8-quinolyl)-ethylenediaminatonickel(II). Recrystallisation from benzene gave small dark violet needles which decomposed at temperatures over 300°C. They are soluble in carbon disulfide with a green colour, in benzene, carbon tetrachloride or chloroform with a blue colour. (Found: N 15.02. Calc. for $C_{30}H_{18}N_4Ni$: N 15.10). The corresponding inner-complexes of copper(II) (violet) and cobalt(II) (red violet) are unstable substances, and their correct analysis could not be ascertained.

N,N'-Bis-(8-quinolyl)-trimethylenediaminatonickel(II). Recrystallisation of the crude product from benzene yielded small violet plates; m.p. 196–205°C. These crystals give a blue solution in chloroform, benzene, ethyl acetate, and light petroleum, a green solution in carbon disulfide and carbon tetrachloride, whilst in dioxane a violet solution is obtained. (Found: N 14.42. Calc. for $C_{31}H_{18}N_4Ni$: N 14.56). The corresponding inner-complex with copper(II) (red) was not isolated with a stoichiometric composition.

N,N'-Bis-(8-quinolyl)-1,3-butanediaminatonickel(II). Recrystallisation from benzene, gave small violet needles; m.p. 216–225°C. These dissolve in ethanol, acetone, chloroform

dioxane, ethyl acetate, carbon tetrachloride and light petroleum to give a blue solution, and in carbon disulfide, to give a green solution. (Found: C 65.80; H 4.97; N 13.63. Calc. for $C_{22}H_{20}N_4Ni$: C 66.20; H 5.05; N 14.01). The corresponding copper(II) compound (red violet) gave repeatedly nitrogen values which were too low.

N,N'-Bis-(quinoline-8-sulfonyl)-ethylenediamine (X). To a solution of ethylenediamine (0.6 g) in pyridine, quinoline-8-sulfonyl chloride (4.55 g) was added slowly with cooling. The reaction mixture was diluted with water and allowed to stand at 0° for 24 h. The crude product was separated by filtration, and recrystallised from pyridine/ethanol mixture to give yellow crystals; m.p. 258–260°C. (Found: C 54.05; H 4.08; N 12.50. Calc. for $C_{20}H_{18}N_4O_4S_2$: C 54.30; H 4.10; N 12.67). This compound did not form metal chelates.

IR-spectrum: 646 vw, 715 m, 769 vw, 792 m, 810 vw, 835 m, 865 vw, 939 vw, 955 vw, 989 w, 1054 vw, 1069 w, 1095 w, 1146 s, 1166 vs, 1215 m, 1240 vw, 1325 vs, 1385 vw, 1427 m, 1460 vw, 1495 m, 1565 w, 1595 w, 1611 w, 3060 w, 3255 m.

Nitroso derivative of N,N'-bis-(8-quinolyl)-ethylenediamine (XIV). *N,N'*-Bis-(8-quinolyl)-ethylenediamine (15.7 g) was dissolved in concentrated hydrochloric acid (200 ml) (warming required) to give a clear solution. After cooling, a solution of sodium nitrite (7.5 g) in water (20 ml) was added with stirring over a period of 20 min. After standing for ½ h at 0° the mixture was made alkaline and the precipitate filtered by suction, washed with water and dried. Yield 16.5 g. Repeated extractions with boiling benzene and precipitation of the benzene extracts with light petroleum (b.p. 35–60°C) gave a 75 % yield of the pure compound. Recrystallisation from ethanol gave white plates, which rapidly turned yellowish in air. M.p. 182–183°C. (Found: C 64.55; H 4.37; N 22.50. Calc. for $C_{20}H_{16}N_6O_2$: C 64.51; H 4.35; N 22.57).

Attempts to reduce this compound to the corresponding dihydrazine with various reducing agents failed completely, the unchanged compound being recovered in all cases.

IR-spectrum: 354 m, 751 m, 787 s, 810 vw, 820 w, 828 m, 856 m, 1023 vw, 1056 vw, 1101 s, 1135 m, 1147 s, 1186 s, 1205 vw, 1242 w, 1253 m, 1319 vw, 1391 s, 1420 m sh, 1430 s, 1449 s, 1500 m, 1570 vw, 1589 w, 3010 vw.

8-Acetamidoquinoline,⁸ *8-benzamidoquinoline*,⁹ and *8-p-toluenesulfonamidoquinoline*¹⁰ were prepared according to the literature.

2-Quinolinecarbaldehyde was prepared following essentially the directions given by Hamer.¹¹ The yield was 58 % of an almost colourless compound melting at 69–70°C (from light petroleum). On evaporating the mother liquor, an additional crop of crystals was obtained, melting at 67–69°C. This made the total yield 70 %.

IR-spectrum: 752 s, 765 m, 774 w, 794 m, 842 s, 883 m, 888 m, 992 w, 1017 w, 1109 m, 1115 w sh, 1151 w, 1207 m, 1234 m, 1267 m, 1302 m, 1312 m, 1337 w, 1433 m, 1462 m, 1506 m, 1569 m, 1592 m, 1614 w, 1641 m, 1705 vs, 2825 m, 3070 m.

*2-Quinolinecarbaldoxime*⁹ (m.p. 185–186°C). An ethanolic solution of this compound gave an olive green precipitate with copper sulfate, and with nickel(II) chloride, gave a strong orange colour on addition of NaOH.

IR-spectrum: 615 w, 740 m, 749 m, 771 vw, 791 m, 830 s, 901 vw, 922 vw, 942 w, 953 w, 1006 vs, 1020 s, 1118 w, 1140 vw, 1207 vw, 1295 w, 1320 w, 1345 m, 1380 w, 1430 s, 1455 m, 1507 vs, 1565 m, 1604 s, 2780 s br, 2900 s br, 3020 m, 3080 m, 3200 s.

Deuteration left the spectrum below 2000 cm^{-1} practically unchanged, whilst the broad 2780 and 2900 cm^{-1} absorptions were notably weakened, with the appearance of two new bands in the 2000–2500 cm^{-1} range. This seems to indicate strongly a chelate structure in which only the chelating hydrogen atom is exchanged with deuterium, on deuteration.

2-Quinolinecarbaldehyde phenylhydrazone^{12,13} (XI) and *p-nitrophenylhydrazone*¹⁴ (XII) had different chelating properties. They both give an intense yellow colour with copper(II) sulfate and nickel(II) chloride, but only the *p*-nitrophenylhydrazone forms deep violet solutions on the addition of NaOH. *2-Quinolinecarbaldehyde thiosemicarbazone*, m.p. 234–237°C (Found: N 24.06. Calc. for $C_{11}H_{10}N_2S$: N 24.34) developed a strong yellow colour with copper(II) and nickel(II) salts, but no difference was observed on addition of NaOH.

*8-Quinolinecarbaldoxime*¹⁵ (m.p. 116–117°C) showed exactly the same colour shifts with metal salts as the 2-oxime.

IR-spectrum: 636 m, 780 s, 790 s, 806 vw, 827 m, 845 m sh, 869 vs, 1034 vw, 1049 w, 1132 vw, 1145 vw, 1166 w, 1204 vw, 1239 vw, 1250 vw, 1289 m, 1306 m, 1317 m, 1365 w, 1470 m sh, 1485 m sh, 1505 s, 1576 w, 1594 w, 1619 w, 2910 m, 3025 m, 3080 s, 3260 vs br.

This oxime behaved entirely different to the 2-oxime on deuteration. All the absorptions in the 2900—3300 cm^{-1} range were weakened, whilst at the same time a new pattern of bands was set up between 2000 and 2500 cm^{-1} . In addition, several new bands appeared in the 700—1600 cm^{-1} range, followed by a general change in the distribution of intensities and a minor shift of the bands. Thus, it can be concluded that in this case the hydrogen atom of the oximino group is replaced in addition to the hydrogen atom at the adjacent carbon atom. For a further discussion of these results, see text.

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