

Studies of Chelates with Heterocyclic Ligands

IV. Transition Metal Complexes with *N*-(8-Quinoly)salicylaldimine

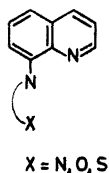
BRITTA MYNSTER DAHL and OTTO DAHL

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

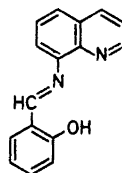
The preparation and properties of some transition metal complexes with the new tridentate ligand *N*-(8-quinoly)salicylaldimine (8-QSH) are reported. Magnetic, conductivity and spectroscopic data indicate an octahedral configuration around the coordinated metal atom in $[M(8-QS)_2]^{(n-2)+}$, $M^{n+} = Mn(II), Fe(III), Co(III), Ni(II),$ and $Zn(II)$. $Fe(III)$ chloride also forms a mono-complex. K_2PdCl_4 dissolved in aqueous methanol leads to hydrolysis of the ligand. $Cu(II)$ halides form square-planar mono-complexes $[CuX(8-QS)]$, $X = Cl$ and Br , which readily coordinate one mole of pyridine. Conductivity and spectroscopic data indicate five-coordination around the copper atom in the pyridine complexes $[CuX(8-QS)Py]$. Copper(II) perchlorate forms a complex $[Cu(8-QS)(8-QSH)]ClO_4$ which also appears to be five-coordinate.

The infrared C=N and C-O stretching frequencies of the ligand and its complexes are assigned. The bands show the expected shifts on coordination.

In previous papers in this series^{1,2} we have investigated the chelating behaviour of 8-aminoquinoline and some of its derivatives towards transition metals. The metal chelate compounds hitherto reported have been derived from bi- or tetradentate ligands. We are now studying the tridentate ligands of general type I derived from 8-aminoquinoline and in this paper we report the preparation and properties of some metal chelate complexes obtained from the new ligand *N*-(8-quinoly)salicylaldimine (8-QSH).



I



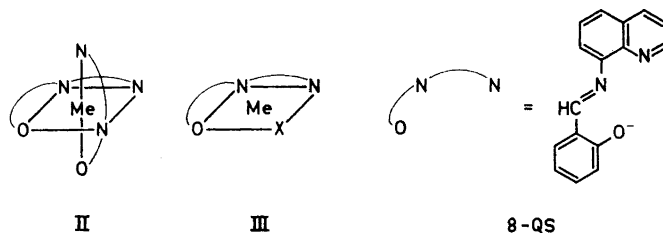
8-QSH

The coordination chemistry of Schiff bases derived from 8-aminoquinoline has been little investigated. The only ligands of this type that have been studied are the compounds derived from 8-aminoquinoline with acetylacetone,³ and with some substituted and unsubstituted pyridine-2-carbaldehydes.⁴⁻⁶

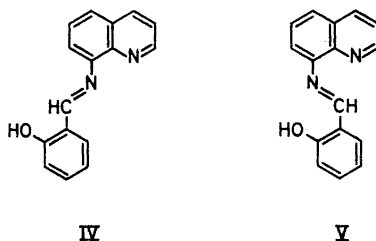
The ligand 8-QSH is readily obtained by condensation of 8-aminoquinoline with salicylaldehyde in ethanol. Interestingly, benzaldehyde under similar conditions reacts with 8-aminoquinoline to give benzylidene-bis-(8-quinolyl-amine) instead of the expected product. The reason for the failure to obtain any Schiff base in this case is at present obscure, but further work on this reaction will be reported later.

The unusual orange-red colour of 8-QSH (λ_{\max} ca. 475 m μ in the solid state) is characteristic for *o*-hydroxyanils and has been attributed to tautomerism involving an *o*-quinoid structure.⁷ The absorption band, responsible for the orange-red colour of 8-QSH, is found at ca. 455 m μ in methanol and dimethylformamide solutions but is not observed in cyclohexane solution. The absence of the band in the latter solvent leads to the conclusion that solvents which can form hydrogen bonds to the solute are essential for the tautomerism to take place, either by providing a route for the hydrogen transfer, or by stabilization of the quinoid tautomer.⁷

8-QSH would be expected to be capable of functioning as a tridentate ligand in complexes derived from the anion *N*-(8-quinolyl)salicylaldimate (8-QS). As the resonance in 8-QS requires approximate planarity, coordination compounds with transition metals are expected to have structures of the type II and III, with octahedral and square-planar coordinated metal atoms, respectively.



The tridentate behaviour of 8-QS, assumed in the above structures, requires some comments. Molecular models show, that when two of the three donor atoms in 8-QS are within bonding distance of a metal atom belonging to the first transition series, the third donor atom is also within bonding distance, provided that 8-QS has the *trans*-configuration around the C=N bond as shown above. The *cis*-form of 8-QSH is expected to be more sterically hindered than the *trans*-isomer and actually only one isomer is obtained in the preparation of 8-QSH. Also, only the *trans*-isomer of 8-QSH will be able to form the intramolecular hydrogen bonds indicated to be present in 8-QSH from the infrared evidence discussed below. However, it is possible for the *trans*-isomer of 8-QSH to act also as a bidentate (or a monodentate) in the conformations IV or V.



8-QSH was reacted with Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) salts in methanol. With Cr(III) salts no pure compound could be obtained, possibly because the ions $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ or $\text{Cr}(\text{CH}_3\text{OH})_6^{3+}$ are so inert that solvolysis of the ligand takes place prior to complex formation. K_2PdCl_4 in cold aqueous methanol on treatment with 8-QSH gave bis-(8-aminoquinoline)palladium(II) chloride⁸ and salicylaldehyde. This result shows that the ligand is hydrolysed under these conditions. A hydrolysis of this kind has been reported in the case of other Schiff bases,⁹ particularly in aqueous solutions in the presence of metal ions which form strong bonds to nitrogen. The coordination leaves the nitrogen atom of the C=N group electron deficient and will thus facilitate the nucleophilic attack of water on the adjacent carbon atom. In addition, palladium(II), having a lower affinity for oxygen compared to nitrogen, will possibly not use the oxygen donor atom in 8-QSH for coordination.

With the exception of Cu(II) salts, all other transition metal salts examined react readily with 2 mol of 8-QSH in the presence of triethylamine to form complexes of the composition $[\text{M}(8\text{-QS})_2] \cdot \text{H}_2\text{O}$ (M=Mn(II), Ni(II), and Zn(II)) or $[\text{M}(8\text{-QS})_2] \text{X} \cdot n \text{H}_2\text{O}$ (M=Fe(III), Co(III), X=Cl, Br, or ClO_4). Triethylamine was added to the preparation mixture in order to neutralize

Table 1. Magnetic and conductivity data for some complexes of *N*-(8-quinolyl)salicylaldimine (8-QSH).

Compound	$\chi_M' \times 10^6$ ^a		μ_{eff} (B.M.)		$\Lambda_M \text{ cm}^2 \text{ ohm}^{-1}$ <i>c</i> = 10^{-3}M , CH_3NO_2
	195°K	293°K	195°K	293°K	
$[\text{Mn}(8\text{-QS})_2] \cdot \text{H}_2\text{O}$	20 570	13 570	5.69	5.70	3
$[\text{FeCl}_2(8\text{-QS})] \cdot \text{CH}_3\text{OH}$	21 210	14 850	5.90	5.90	14
$[\text{Fe}(8\text{-QS})_2] \text{Cl} \cdot 2 \text{H}_2\text{O}$	19 930	13 600	5.60	5.67	84
$[\text{Co}(8\text{-QS})_2] \text{Cl} \cdot \text{H}_2\text{O}$		170		0	81
$[\text{Ni}(8\text{-QS})_2] \cdot \text{H}_2\text{O}$	5 810	3 980	3.03	3.07	1
$[\text{CuCl}(8\text{-QS})] \cdot \text{CH}_3\text{OH}$	2 080	1 460	1.81	1.86	0
$[\text{CuCl}(8\text{-QS})]$	1 880	1 290	1.72	1.75	0
$[\text{CuCl}(8\text{-QS})\text{Py}]$	2 020	1 370	1.78	1.80	1
$[\text{Cu}(8\text{-QS})(8\text{-QSH})] \text{ClO}_4$	2 290	1 620	1.90	1.96	91
$[\text{Zn}(8\text{-QS})_2] \cdot \text{H}_2\text{O}$					2

^a Corrected for diamagnetism.²⁴

the hydrogen ions liberated by complex formation. The water molecules present in the compounds are presumably not coordinated, since dehydration of the complexes did not cause any change in their infrared spectra in the 1000 cm^{-1} region. Coordinated water is reported to exhibit a band in this region.²

From the following discussion it is concluded that all the bis-complexes have the two 8-QS ligands octahedrally coordinated around the metal atom, *i.e.* that they possess the structure II. Thus, the electrical conductivities in nitromethane (Table 1) correspond to the above formulas, and the magnetic moments (Table 1) have the values typical for the metals in octahedral environments.¹⁰ The absorption spectra of the compounds (Table 2) are of limited value in determining the stereochemistry around the metal atoms, because

Table 2. Absorption spectra for some complexes of *N*-(8-quinolyl)salicylaldimine (8-QSH).

Compound	State	Absorption maxima, $\text{cm}^{-1} \times 10^{-3}$ (ϵ_M for soln. ^a)
[Mn(8-QS) ₂].H ₂ O	solid DMF ^b	11.5 sh, 17.5 sh, 20.8 sh, 24.4 17.3 sh (360), 22.4 (28 100)
[FeCl ₂ (8-QS)].CH ₃ OH	solid DMF	14 sh, 19 sh, 24.7 (broad wing), 24.7 (9 800)
[Fe(8-QS) ₂]Cl.2 H ₂ O	solid DMF	12 sh, 20 sh, 25.0 (broad wing), 24.6 (15 200)
[Co(8-QS) ₂]Cl.H ₂ O	solid DMF	15.5 sh, 19.4 sh, 21.5 15.5 sh (140), 22.0 (13 300)
[Ni(8-QS) ₂].H ₂ O	solid DMF	12.0, 19.2 sh, 23.5 12.0 (50), 20.8 (29 000)
NiCl ₂ (8-QSH). $\frac{1}{2}$ H ₂ O	solid	10.6, 15.6, 25.0
[CuCl(8-QS)].CH ₃ OH	solid DMF	15.4, 21.5 15.3 (150), 22.3 (11 400)
[CuCl(8-QS)]	solid	15.8, 21.5 sh, 24.4
[CuCl(8-QS)Py]	solid DMF	11 sh, 16.0, 20.4, 21.8 sh, 23.5 15.4 (150), 22.4 (11 400)
[CuBr(8-QS)].CH ₃ OH	solid	15.9, 21.0 sh, 23.8
[CuBr(8-QS)Py]	solid	11.4 sh, 16.4, 21.0 sh, 23.3
[Cu(8-QS)(8-QSH)]ClO ₄	solid	13.0 sh, 16.2, 21.2 sh, 22.5

^a ϵ -values for shoulders are the apparent values, not corrected for contributions from the wing of the more intense band.

^b DMF = dimethylformamide.

most $d-d$ transitions appear only as ill-defined shoulders on the low frequency side of the wing of the strong ligand absorption band around $22\,000\text{ cm}^{-1}$. Only the Ni(II) complex shows a distinct band at $12\,000\text{ cm}^{-1}$ in addition to a shoulder at $19\,000\text{ cm}^{-1}$. These two bands are assigned¹¹ to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ($12\,000\text{ cm}^{-1}$) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ($19\,200\text{ cm}^{-1}$) of octahedrally coordinated Ni(II). The positions are close to those found for tris-(8-aminoquinoline)nickel(II) chloride.² The Co(III) complex shows a shoulder at $15\,500\text{ cm}^{-1}$ which is assigned¹² to one of the spin-forbidden transitions ${}^1A_{1g} \rightarrow {}^3T_{1g}$ or ${}^3T_{2g}$ in octahedral environments, the lowest allowed transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ being the shoulder at $19\,400\text{ cm}^{-1}$.¹² In the Fe(III) complex, the wing of the ligand band is much broader than for the other complexes, no doubt due to the superposition of a charge-transfer band in the visible region, and therefore no assignments are attempted for the two broad shoulders found in the reflectance spectrum. Finally the band at *ca.* $11\,500\text{ cm}^{-1}$ in the reflectance spectrum of the Mn(II) complex is most likely due to impurities.

Attempts to prepare complexes of the above metals with a 1:1 ligand to metal ratio did not generally result in pure compounds. However, a methanolic FeCl_3 solution gave a well defined compound with the composition $\text{FeCl}_2(8\text{-QS})\cdot\text{CH}_3\text{OH}$. The molar conductance in nitromethane (Table 1) is low, indicating coordination of both chlorine atoms. The magnetic moment corresponds to a high-spin complex with no intermolecular magnetic interactions. The methanol molecule is easily removed by heating *in vacuo* and is therefore presumably not coordinated. The low solubility of the complex precludes molecular weight determination, and therefore a distinction could not be made between the two remaining possibilities, a five-coordinated monomeric structure or an octahedral dimeric structure.

When triethylamine was not added, most of the metal salts when treated with 8-QSH gave compounds with variable compositions. In the case of Ni(II) chloride, however, a yellow compound with the composition $\text{NiCl}_2(8\text{-QSH})\cdot\frac{1}{2}\text{H}_2\text{O}$ could be obtained from acetone-ethanol solution. The reflectance spectrum (Table 2) showed two weak bands in accordance with an octahedral coordination.¹¹ The presence of strong NH^+ absorptions and the absence of OH absorptions in the infrared spectrum indicate that the phenolic hydrogen is transferred to the ring nitrogen in the complex and the ligand therefore acts as a bidentate only (conformation V). When treated with triethylamine, the complex is converted to the aforementioned red complex $[\text{Ni}(8\text{-QS})_2]\cdot\text{H}_2\text{O}$ and NiCl_2 .

Copper(II) halides in methanol formed complexes with the composition $\text{CuX}(8\text{-QS})\cdot\text{CH}_3\text{OH}$, $\text{X}=\text{Cl}$ and Br . Recrystallization from nitrobenzene gave the methanol-free complexes. Recrystallization from dimethylformamide-pyridine mixtures resulted in complexes with the composition $\text{CuX}(8\text{-QS})\cdot\text{Py}$. The compounds are all green and are non-electrolytes in nitromethane (Table 1). The magnetic moments (Table 1) correspond to magnetically dilute compounds.¹⁰ The absorption spectra (Table 2 and Fig. 1) all show a band at about $15\,500\text{ cm}^{-1}$ but the pyridine complexes have in addition a broad shoulder around $11\,000\text{ cm}^{-1}$. As pyridine does not absorb in this region, the observed change in the spectra must be due to changes in the d -orbitals around the copper atom, caused by coordination of pyridine. The shoulder is frequently found in spectra of five-coordinated Cu(II) complexes, *e.g.* $\text{Cu}(\text{NH}_3)_5^{2+}$,¹³

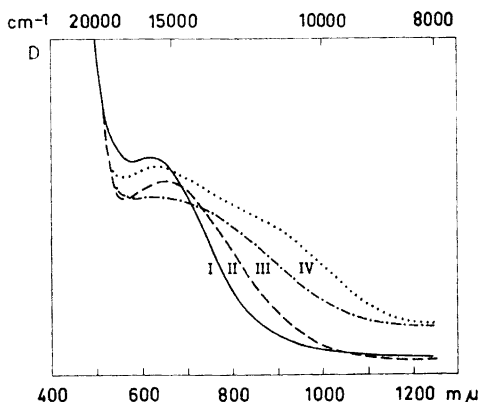
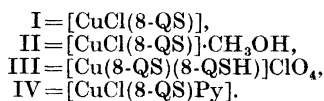


Fig. 1. Reflectance spectra of copper *N*-(8-quinolyl)salicylaldimine (8-QSH) complexes.



[Cu(trenMe)X]⁺,¹⁴ and several salicylaldimine complexes,^{15,16} but is generally absent in square-planar compounds. The pyridine complexes are therefore formulated [CuX(8-QS)Py] with five-coordinated copper, whilst the methanol complexes and the solvent-free complexes presumably are square-planar coordinated (structure III). A definite proof of the proposed structures, however, is not possible without an X-ray structure determination. Some analogous adducts of salicylaldimine Cu(II) complexes with pyridine¹⁷ or water¹⁸ have been shown by X-ray structure determinations to contain five-coordinated copper, the additional ligand being at the apex of a square pyramid.

When heated to about 160°C the copper complexes gave off methanol or pyridine accompanied by a colour change from green to olive. The green complexes [CuX(8-QS)], obtained from nitrobenzene, however, are olive also when powdered, so there is no reason to believe that the different colours correspond to isomers; *cf.* the green and brown isomers of other salicylaldimine Cu(II) complexes.¹⁹

The reaction of copper(II) perchlorate with 8-QSH in aqueous methanol gave a complex with the stoichiometry Cu(8-QS)(8-QSH)ClO₄. The infrared spectrum (KBr) has a rather sharp OH absorption at 3280 cm⁻¹ in accordance with the formulation of the complex as containing 8-QSH. The two strong perchlorate absorptions at *ca.* 1080 cm⁻¹ and 630 cm⁻¹ show some splitting, but no perchlorate band at *ca.* 940 cm⁻¹, indicative of coordinated ClO₄,²⁰ was found, and the compound behaved as an 1:1 electrolyte in nitromethane (Table 1). The perchlorate ion is therefore coordinated neither in the solid state nor in solution. The reflectance spectrum (Table 2 and Fig. 1) shows the shoulder which is considered characteristic for five-coordinated Cu(II), and the complex is accordingly formulated [Cu(8-QS)(8-QSH)]ClO₄ with an uncoordinated OH group and presumably five-coordinated copper. An uncoordinated OH group is possible if the 8-QSH is coordinated in the conformation IV. When base was added to a methanolic solution of the complex, a red-brown precipitate was obtained. Repeated preparations showed variable compositions, and infrared spectra invariably showed the presence of perchlorate ions, which could not be removed by recrystallization. If the OH

group in $[\text{Cu}(8\text{-QS})(8\text{-QSH})]\text{ClO}_4$ is coordinated, the octahedral compound $[\text{Cu}(8\text{-QS})_2]$ should be easily obtainable, because, due to the withdrawal of electrons by the metal atom, a coordinated OH group should be more acidic than the free group. This result therefore supports the formulation of the perchlorate complex as containing uncoordinated OH.

Infrared spectra. The infrared spectra of 8-QSH and its metal complexes show a rather complex pattern with many strong absorption bands, especially in the $1300\text{--}1600\text{ cm}^{-1}$ region. Some of the more important bands have been assigned and are tabulated in Table 3.

Table 3. Infrared O—H, C=N and C—O frequencies of *N*-(8-quinolyl)salicylaldimine (8-QSH) and some coordination compounds.

Compound (in KBr)	O—H stretching, cm^{-1}		C=N stretching cm^{-1}	C—O stretching cm^{-1}
	$\text{H}_2\text{O}/\text{CH}_3\text{OH}$	phenolic		
8-QSH	—	—	1617 vs 1624 vs <i>a</i>	1276 m, 1287 sh 1283 m <i>a</i>
<i>N</i> -(1-naphthyl)-salicylaldimine	—	—	1615 vs 1623 vs <i>a</i>	1279 s 1282 s <i>a</i>
8-(2-hydroxybenzyl-amino)quinoline	—	2800—3200	—	1270 m
	—	3000—3400 <i>b</i>	—	<i>c</i>
8-QSLi	—	—	1614 vs	1348 m
$[\text{Mn}(8\text{-QS})_2]\cdot\text{H}_2\text{O}$	3410 m br	—	1608 vs	1315 m
$[\text{FeCl}_2(8\text{-QS})]\cdot\text{CH}_3\text{OH}$	3440 m br	—	1602 vs	1315 m
$[\text{Fe}(8\text{-QS})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	3420 m br	—	1607 vs	1318 s
$[\text{Co}(8\text{-QS})_2]\text{Cl}\cdot\text{H}_2\text{O}$	3420 m br	—	1612 vs	1318 s br
$[\text{Ni}(8\text{-QS})_2]\cdot\text{H}_2\text{O}$	3400 w br, 3325 w	—	1607 vs, 1610 sh	1316 m
$[\text{CuCl}(8\text{-QS})]\cdot\text{CH}_3\text{OH}$	3414 m br	—	1613 vs	1322 sh, 1330 m
$[\text{Cu}(8\text{-QS})(8\text{-QSH})]\text{ClO}_4$	—	3280 m	1608 vs	1267 m, 1312 m, 1328 m
$[\text{Zn}(8\text{-QS})_2]\cdot\text{H}_2\text{O}$	3460 m br	—	1611 vs	1318 m

^a In CCl_4 solution. ^b In CH_2Cl_2 solution. ^c Masked by solvent absorption.

In 8-QSH, the O—H stretching absorption is not observed when the spectra are recorded in KBr, whilst in CCl_4 solution it appears as a very broad band centered around 2800 cm^{-1} . This very low position has been found for other *o*-hydroxyanils^{21,22} and is attributed to strong intramolecular hydrogen bonding. The only complex prepared which still contains the phenolic hydrogen is the copper perchlorate complex. In this compound the intramolecular hydrogen bonding is made impossible by complex formation, and accordingly the O—H stretching absorption is found as a well defined band at 3280 cm^{-1} , a normal position for intermolecular bonded hydroxyl groups.

The C=N stretching vibration is assigned to the very strong absorption found in the region 1602–1624 cm^{-1} . This assignment is in agreement with the literature^{21,22} and is confirmed by the absence of the band in 8-(2-hydroxybenzylamino)quinoline and by its shift to lower frequencies on complex formation. The shifts are only small, but similar small shifts are found for other Schiff base complexes.^{21,23}

The C—O stretching frequency is found at *ca.* 1280 cm^{-1} in the spectrum of 8-QSH. The corresponding band is found at 1270 cm^{-1} in 8-(2-hydroxybenzylamino)quinoline, at *ca.* 1280 cm^{-1} in *N*-(1-naphthyl)salicylaldimine, and is absent in *N*-(1-naphthyl)benzaldimine. On complex formation, the band is shifted to 1315–1330 cm^{-1} , and in the lithium salt it is found at 1348 cm^{-1} . These shifts are in accordance with an increased double-bond character in the C—O bond as the oxygen atom becomes negatively charged, and the shift is greatest for the lithium salt where the O—M bond presumably is mainly ionic. The copper perchlorate complex shows C—O stretching absorptions in the regions corresponding to both coordinated C—O and uncoordinated C—OH in accordance with the proposed structure. Kovacic²¹ has similarly assigned the C—O frequency for several salicylidene anils and their copper complexes to the regions 1260–1288 cm^{-1} and 1310–1330 cm^{-1} for free and coordinated anils, respectively.

EXPERIMENTAL

The analyses were carried out in the microanalysis department of this laboratory. The magnetic susceptibilities (Table 1) were measured at three field strengths and were independent of the field strength. Electrical conductances (Table 1) were measured in nitromethane on a Radiometer type CDM 2 Conductivity Meter and corrected for the small conductivity of the solvent (2–3 μhos after purification according to Sutton²⁵). The visible spectra (Table 2) were recorded on a Perkin-Elmer Model 137 UV Ultraviolet-Visible Spectrophotometer, or, below 13 000 cm^{-1} , on a Cary Model 14 Spectrophotometer. The reflectance spectra (Table 2) were recorded on a Beckman Spectrophotometer DU Model G 2400. Infrared spectra were obtained on a Perkin-Elmer model 337 Grating Infrared Spectrophotometer.

N-(8-Quinolyl)salicylaldimine (8-QSH). 8-Aminoquinoline (0.1 mol) and salicylaldehyde (0.1 mol) were refluxed for 4 h in abs. ethanol (80 ml). The solvent was evaporated and the sticky red residue treated with dry ether (60 ml). The crystalline compound which separated by cooling in dry-ice and scratching was washed with ether and pentane and finally dried *in vacuo*. The crude product (yield 60–70 %), which melted at 67–72°C, was sufficiently pure for preparation of the complexes. After two recrystallizations from dry ether the pure, orange-red compound melted at 72.5–73.5°C. (Found: C 77.10; H 5.09; N 11.35. Calc. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$: C 77.39; H 4.87; N 11.28).

N-(1-Naphthyl)salicylaldimine. The compound was prepared according to Senior and Shephard.²⁶ After two recrystallizations from methanol the light yellow compound melted at 42.5–43.5°C (lit.²⁶ 45.5°C). (Found: C 82.74; H 5.41; N 5.60. Calc. for $\text{C}_{17}\text{H}_{13}\text{NO}$: C 82.57; H 5.30; N 5.66). The high-melting form described by Alphen and Drost²⁷ was not obtained.

Benzylidene-bis-(8-quinolylamine). 8-Aminoquinoline (0.01 mol) and benzaldehyde (0.01 mol) were mixed with ethanol (2 ml) and refluxed for 4 h. An IR-spectrum (CCl_4) of the crude oil, obtained after evaporation of the solvent, showed no C=N stretching absorption. The crude product was dissolved in ether and precipitated with pentane. After two reprecipitations the light yellow compound (30–40 % yield) melted at 86–91°C. Recrystallization from toluene-pentane furnished light yellow crystals, m.p. 92–93.5°C. (Found: C 79.90; H 5.45; N 14.65. Calc. for $\text{C}_{22}\text{H}_{20}\text{N}_4$: C 79.76; H 5.36; N 14.88). The IR-spectrum (KBr) showed N—H stretching absorptions at 3405 cm^{-1} (s) and 3415 cm^{-1} (sh).

N-(1-Naphthyl)benzalimine. 1-Naphthylamine and benzaldehyde were refluxed for 2 h in abs. ethanol. The solution was diluted with pentane and set aside for crystallization. After 24 h the crystals formed were filtered off, washed with ethanol and recrystallized from ethanol. The light brown crystals melted at 72.5–73°C (lit.²⁶ 73–75°C).

Lithium N-(8-quinolyl)salicylaldiminato. To a solution of 8-QSH (1 mmol) in methanol (5 ml) was added LiOH·H₂O (1.5 mmol) in methanol (2 ml). The yellow-orange salt, which precipitated quickly, was washed with methanol and dried *in vacuo*. The compound (yield 50 %) decomposes on heating above 250°C. (Found: C 75.35; H 4.52; N 11.17. Calc. for C₁₆H₁₁LiN₂O: C 75.61; H 4.36; N 11.02).

The following complexes have no well-defined melting points, but decompose on heating above ca. 250°C. They all have a rather low solubility in methanol and nitromethane and are insoluble in chloroform and less polar solvents.

Bis-(*N*-(8-quinolyl)salicylaldiminato)manganese(II) hydrate. A solution of 8-QSH (2 mmol) in methanol (15 ml) was mixed with a solution of MnCl₂·4 H₂O (1 mmol) in methanol (10 ml) and triethylamine (2 mmol) was added. After standing overnight, the brown crystals formed were filtered off, washed with methanol and dried *in vacuo*. Yield 75 %. (Found: C 67.70; H 4.12; Cl 0; N 10.02. Calc. for C₃₂H₂₄MnN₄O₃: C 67.72; H 4.26; N 9.88). On heating, the water molecule is given off at ca. 55°C without change in the colour of the complex.

Dichloro-N-(8-quinolyl)salicylaldiminatoiron(III). A solution of 8-QSH (1 mmol) in methanol (10 ml) was mixed with a solution of FeCl₃ (1 mmol) in methanol (7.5 ml). The mixture was allowed to stand for one day. The blue-black crystals were washed with methanol and ether and dried *in vacuo*. Yield 90 % of the *methanol adduct*. (Found: C 50.35; H 3.72; Cl 17.07. Calc. for C₁₇H₁₅Cl₂FeN₂O₂: C 50.28; H 3.72; Cl 17.46). On heating to 100°C *in vacuo* for 2 h the black *methanol-free complex* was formed. (Found: C 51.60; H 3.04; Cl 18.84; N 7.57. Calc. for C₁₆H₁₁Cl₂FeN₂O: C 51.39; H 2.96; Cl 18.95; N 7.49).

Bis-(*N*-(8-quinolyl)salicylaldiminato)iron(III) chloride dihydrate. 8-QSH (2 mmol) in methanol (30 ml), FeCl₃ (1 mmol) in methanol (20 ml) and triethylamine (2 mmol) gave after standing overnight a 60 % yield of small, dark brown crystals. (Found: C 61.60; H 4.31; Cl 5.70; N 9.06. Calc. for C₃₂H₂₆ClFeN₄O₄: C 61.80; H 4.22; Cl 5.70; N 9.01). Water is given off on heating the complex to about 150°C without change in the colour.

Bis-(*N*-(8-quinolyl)salicylaldiminato)cobalt(III) chloride hydrate. 8-QSH (2 mmol) in methanol (20 ml) and CoCl₂·6 H₂O (1 mmol) in methanol (15 ml) gave after 4 h a 60 % yield of red-brown crystals. (Found: C 63.15; H 4.19; Cl 5.59. Calc. for C₃₂H₂₄ClCoN₄O₃: C 63.21; H 4.15; Cl 5.83). The water molecule is given off above 90°C without change in the colour of the complex.

Treatment of the above two complexes with lithium bromide or lithium perchlorate in methanol yielded the corresponding bromide and perchlorate complexes. They have the same colours as the chloride complexes.

Attempts to prepare Co(II) or Fe(II) complexes under a nitrogen atmosphere using degassed solvents failed. Only the above Co(III) and Fe(III) complexes could be obtained. The identity with the above complexes was ascertained by 1) analysis, 2) a strong, red colour with KSCN after decomposition of the iron complex with hydrogen chloride in water, 3) the absence of OH stretch absorptions in the infrared spectra of the dried complexes, and 4) the diamagnetism of the cobalt complex. The above experiments indicate that the ligand is able to oxidize Co(II) and Fe(II) to the trivalent oxidation state.

N-(8-Quinolium)salicylaldiminatonickel(II) chloride semihydrate. 8-QSH (1 mmol) in acetone (10 ml) was mixed with NiCl₂·6 H₂O (1 mmol) in abs. ethanol (5 ml). The yellow complex, which separated immediately in nearly quantitative yield, was washed with abs. ethanol and dried *in vacuo*. The water was not given off on prolonged heating at 150°. (Found: C 49.65; H 3.65; Cl 18.32; N 7.24. Calc. for C₁₆H₁₃Cl₂N₂NiO_{3/2}: C 49.67; H 3.39; Cl 18.32; N 7.24). The infrared spectrum (KBr) show strong, broad absorptions at 2580–2900 cm⁻¹ due to N⁺–H stretching vibrations.

Bis-(*N*-(8-quinolyl)salicylaldiminato)nickel(II) hydrate. 8-QSH (2 mmol) in methanol (50 ml), NiCl₂·6 H₂O (1 mmol) in methanol (30 ml) and triethylamine (2 mmol) were mixed to give a clear, red solution. After standing overnight, the crystals formed were filtered off, washed with methanol and dried *in vacuo*. Yield 75 % of red-brown crystals with a green lustre. (Found: C 67.10; H 4.35; Cl 0; N 9.62. Calc. for C₃₂H₂₄N₄NiO₃: C 67.26;

H 4.24; N 9.81). The water molecule is given off without any colour change on heating the hydrate above 160°C.

Chloro-N-(8-quinolyl)salicylaldiminatocopper(II)-methanol. 8-QSH (1 mmol) in methanol (10 ml) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) in methanol (10 ml) were mixed. The complex, which separated quickly, was washed with methanol and dried *in vacuo*. Yield 80 % of dark olive-green crystals. (Found: C 53.70; H 3.76; Cl 9.44; N 7.66. Calc. for $\text{C}_{17}\text{H}_{15}\text{ClCuN}_2\text{O}_2$: C 53.98; H 4.00; Cl 9.37; N 7.40).

Chloro-N-(8-quinolyl)salicylaldiminatocopper(II). Recrystallization of the methanol complex from nitrobenzene resulted in green crystals of the methanol-free complex. (Found: C 55.55; H 3.28; Cl 10.05; N 8.15. Calc. for $\text{C}_{16}\text{H}_{11}\text{ClCuN}_2\text{O}$: C 55.51; H 3.20; Cl 10.23; N 8.09). When powdered the colour is olive. The same complex was obtained on heating the methanol complex to 180°C for 1 h. The crystals crumble and the colour turns olive. (Found: C 55.40; H 3.17; Cl 10.14; N 8.16).

Chloro-N-(8-quinolyl)salicylaldiminato-pyridinecopper(II). The methanol complex (1 mmol) was dissolved in a hot mixture of pyridine (5 ml) and dimethylformamide (20 ml) to give a brown, clear solution. The complex which crystallized on cooling was washed with dimethylformamide and ether and dried *in vacuo*. Yield 90 % of green crystals. (Found: C 59.05; H 3.93; Cl 8.48; N 9.94. Calc. for $\text{C}_{21}\text{H}_{16}\text{ClCuN}_3\text{O}$: C 59.29; H 3.79; Cl 8.34; N 9.88). The pyridine molecule is given off on heating the complex above 160°C. The complex is stable at room temperature.

Bromo-N-(8-quinolyl)salicylaldiminatocopper(II)-methanol. 8-QSH (1 mmol) in methanol (15 ml) and CuBr_2 (1 mmol) in methanol (10 ml) gave a 90 % yield of dark green crystals. (Found: C 48.20; H 3.63; Br 19.15; N 6.74. Calc. for $\text{C}_{17}\text{H}_{15}\text{BrCuN}_2\text{O}_2$: C 48.30; H 3.57; Br 18.90; N 6.63).

Bromo-N-(8-quinolyl)salicylaldiminatocopper(II). Recrystallization of the above complex from nitrobenzene gave green crystals of the solvent-free complex. The same compound was obtained on heating the methanol complex to 180°C for 1 h. (Found: C 49.40; H 2.90; Br 20.30; N 7.12. Calc. for $\text{C}_{16}\text{H}_{11}\text{BrCuN}_2\text{O}$: C 49.18; H 2.84; Br 20.45; N 7.17).

Bromo-N-(8-quinolyl)salicylaldiminato-pyridinecopper(II). This complex was prepared in the same way as the chloro compound. Yield 85 % of dark green crystals. (Found: C 53.75; H 3.51; Br 17.20; N 8.96. Calc. for $\text{C}_{21}\text{H}_{16}\text{BrCuN}_3\text{O}$: C 53.69; H 3.43; Br 17.01; N 8.94).

N-(8-quinolyl)salicylaldiminato-N-(8-quinolyl)salicylaldiminecopper(II) perchlorate. A hot solution of 8-QSH (2 mmol) in methanol (15 ml) was mixed with a hot solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in water (3 ml). The complex crystallized slowly on cooling. After 2 h the crystals were filtered off, washed with methanol and dried *in vacuo*. Yield 70 % of dark olive crystals. (Found: C 58.34; H 3.63; Cl 5.50; N 8.60. Calc. for $\text{C}_{32}\text{H}_{23}\text{ClCuN}_4\text{O}_6$: C 58.36; H 3.52; Cl 5.38; N 8.51). IR-spectrum (KBr, cm^{-1}): 3280 m (OH), 1090 vs, 1060 vs, 633 s, 625 m (ClO_4^-).

Bis-(N-(8-quinolyl)salicylaldiminato)zinc(II) hydrate. 8-QSH (2 mmol) and triethylamine (2 mmol) in methanol (40 ml) was mixed with ZnCl_2 (1 mmol) in methanol (20 ml). The complex started to crystallize after a short time. After 1 h, the golden crystals were filtered off, washed with methanol and dried *in vacuo*. Yield 75 %. (Found: C 66.61; H 4.12; Cl 0; N 9.73. Calc. for $\text{C}_{32}\text{H}_{23}\text{N}_4\text{O}_3\text{Zn}$: C 66.48; H 4.19; N 9.69). On heating, the water is given off above 200°C accompanied by a colour deepening.

Acknowledgement. The authors wish to thank Professor K. A. Jensen for his encouragement to undertake this study, and for valuable suggestions during the work.

REFERENCES

1. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **18** (1964) 1.
2. Nielsen, P. H. and Dahl, O. *Acta Chem. Scand.* **20** (1966) 1113.
3. Lions, F. and Martin, K. V. *J. Am. Chem. Soc.* **80** (1958) 3858.
4. Dwyer, F. P., Gill, N. S., Gyarfas, E. C. and Lions, F. *J. Am. Chem. Soc.* **75** (1953) 3834.
5. Lions, F. and Martin, K. V. *J. Am. Chem. Soc.* **79** (1957) 2733.

6. Goodwin, H. A. and Lions, F. J. *Am. Chem. Soc.* **81** (1959) 6415.
7. Ledbetter, J. W. *J. Phys. Chem.* **70** (1966) 2245.
8. Gustin, V. K. and Sweet, T. R. *Anal. Chem.* **35** (1963) 44.
9. Dekkers, J. and Goodwin, H. A. *Australian J. Chem.* **19** (1966) 2241.
10. Figgs, B. N. and Lewis, J. *Progr. Inorg. Chem.* **6** (1964) 38.
11. Asmussen, R. W. and Bostrup, O. *Acta Chem. Scand.* **11** (1957) 1097.
12. Linhard, M. and Weigel, M. *Z. Phys. Chem.* **11** (1957) 308.
13. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. K. *Acta Chem. Scand.* **8** (1954) 1275.
14. Ciampolini, M. and Nardi, N. *Inorg. Chem.* **5** (1966) 41.
15. Sacconi, L. and Bertini, I. *J. Am. Chem. Soc.* **88** (1966) 5180.
16. Sacconi, L., Ciampolini, M. and Speroni, G. P. *J. Am. Chem. Soc.* **87** (1965) 3102.
17. Hall, D., Sheat, S. V. and Waters, T. N. *Chem. Ind. (London)* **1965** 1428.
18. Llewellyn, F. J. and Waters, T. N. *J. Chem. Soc.* **1960** 2639.
19. Waters, T. N. and Hall, D. *J. Chem. Soc.* **1959** 1200, 1203.
20. Ross, S. D. *Spectrochim. Acta* **18** (1962) 225.
21. Kovacic, J. E. *Spectrochim. Acta* **A 23** (1967) 183.
22. Freedman, H. H. *J. Am. Chem. Soc.* **83** (1961) 2900.
23. Teyssie, P. and Charette, J. J. *Spectrochim. Acta* **19** (1963) 1407.
24. Lewis, J. and Wilkins, R. G. *Modern Coordination Chemistry*, Interscience, New York 1960, p. 403.
25. Sutton, G. J. *Australian J. Chem.* **12** (1959) 637.
26. Senier, A. and Shepheard, F. G. *J. Chem. Soc.* **95** (1909) 441.
27. van Alphen, J. and Drost, G. *Rec. Trav. Chim.* **67** (1948) 622.
28. Crossley, M. L., Dreisbach, P. F., Hofmann, C. M. and Parker, R. P. *J. Am. Chem. Soc.* **74** (1952) 573.

Received October 21, 1968.