

Synthesis, Stability Constant Determination, and Structural Study of Some Complexes of a Zinc Triad Containing Pyridyl-amine-quinoline and Pyridyl-thio-quinoline

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The potentially fluorescent and terdentate ligands containing nitrogen or sulfur as coordinating atom were synthesized and used in the formation of perchlorate or chloride complexes of the metals of the Zn triad. The reaction of the ligands with metal perchlorate salts yields the corresponding bis-chelate derivatives, whereas the same ligands react with metal chloride salts to give monochelate complexes. All of these complexes undergo NMR-scale fast fluxional rearrangement in solution. Some structural X-ray diffractometric studies were also performed and the ensuing data confirm the surmised structures and the solution rearrangement in the case of monochelate substrates and of one Hg derivative, respec-

tively. The equilibrium constants of formation in the case of monochelate derivatives were also determined in water by means of spectrophotometric titration of the studied ligand with the metal ions. The values of the equilibrium constants were confirmed by supplementary determination taking into account the exchange between two different metals and/or dissociation equilibria. The fluorescence activity of ligands and complexes was eventually studied and notably one fluorescent silent ligand gives rise to fluorescent zinc derivatives.

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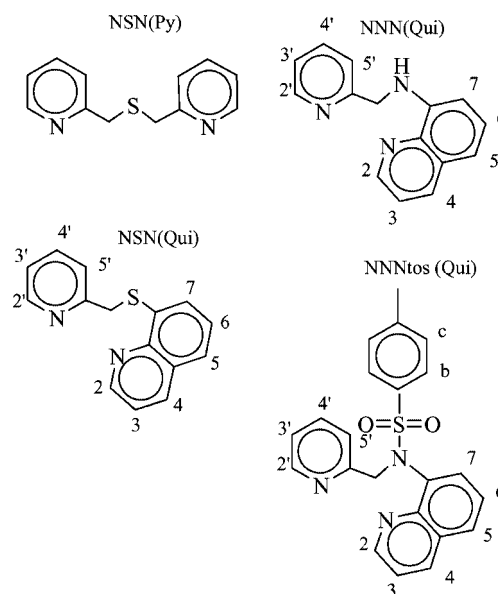
Introduction

The bioactivity of group-12 metal ions is well known, the toxic effects of mercury and cadmium on living organisms being widely recognized.^[1] On the contrary zinc is present in traces in many enzymes and consequently it must be considered a bio-compatible metal at least when its concentration is confined within the millimolar range.^[2] High concentrations of zinc could, however, entail pollution problems when industrial or human wastes in restricted areas are involved.

In this respect, the synthesis of new ligands with remarkable coordinating capabilities represents an important step for the development of chemical devices for the field monitoring of several metal ions.^[3–10] For this reason, we decided to synthesize a series of new polydentate ligands and test their versatility in the identification of the group-12 metals when present in different concentrations and situations.

The synthesized ligands are reported in Scheme 1. We chose to analyze the coordinating capability of the ligands

toward proton and metals in distilled water and in the presence of chloride ions since we aim at using these substrates directly in marine or lagoon waters.



Scheme 1.

It is well known that quinoline displays remarkable properties as a photophysical fluorescent chromophore^[11] and as a coordinating agent towards many transition-metal ions.

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Therefore, the synthesis of polydentate ligands bearing quinoline together with other potentially coordinating atoms could represent an important target in a strategy aiming at low cost and easy identification of several analytes.

Results and Discussion

General Remarks

Owing to the low solubility of the ligands and related complexes in water, all determinations of equilibrium constants were performed without ionic strength control since any addition of inert salt induces massive precipitation under our experimental conditions (i.e. the solubility of the Hg complexes in 0.01 M NaClO₄ dramatically drops to about 1×10^{-6} mol dm⁻³). For this reason we have determined the complex formation equilibrium constants by means of the UV/Vis technique, any potentiometric approach being inadequate. We therefore chose to privilege the use of water as solvent instead of controlling the ionic strength in mixed solvents since we expect that the ligands we synthesized should be used as metal probes in natural and waste waters.

Synthesis of the Ligands

The ligands NSN(Py) {NSN(Py) = 2-[(2-pyridylmethyl)thio]pyridine},^[12a] NNNtos(Qui) [NNNtos(Qui) = 8-*N*-tosyl-*N*-(2-pyridylmethyl)quinoline] and NSN(Qui) [NSN(Qui) = 8-[(2-pyridylmethyl)thio]quinoline], were synthesized according to published procedures;^[12b] the ligand NNN(Qui) {NNN(Qui) = 8-[(2-pyridylmethyl) amino]quinoline} was obtained by removing the tosyl group from the NNNtos(Qui) moiety by acid hydrolysis with concentrated H₂SO₄ at 110 °C.

Synthesis of the Complexes

Bis-Chelate Complexes

Addition of the perchlorate salt M(ClO₄)₂ (M = Zn, Cd, Hg) to the ligand LL'L'' [LL'L'' = NNN(Qui), NNNtos(Qui), NSN(Qui)] in acetonitrile or methanol yields the corresponding complex of general formula [M(LL'L'')₂](ClO₄)₂.

The complexes of Hg and Cd with the ligand NSN are characterized by the down-field shift of the CH₂S protons and the concomitant high-field shift of the aromatic protons H² and H^{2'}. This phenomenon had already been observed,^[13] and was traced back to the interactions occurring between the ring currents of the opposite rings of the bis-coordinated ligand. A down-field shift of the aromatic protons would be otherwise observed upon ligand coordina-

tion. Moreover, in these complexes the CH₂S protons resonate as a singlet and no (¹⁹⁹Hg¹H) and (^{111/113}Cd¹H) coupling even at the lowest temperature achievable (233 K) was observed. The lack of any observable coupling constants could be traced back to the small value of the constant itself or to the rapid exchange of the ligand among complexes. The authors, however, on the basis of their own experience with these kinds of ligands and according to previous observations,^[14] are inclined to believe that the ligands in these cases are not firmly bound to the central metal and that a fluxional rearrangement affects these complexes in solution. As a matter of fact, the solid-state structure of the complex [Hg(NSN)₂(OCIO₃)]ClO₄ was clearly produced by the displacement of one terminus of the potentially terdentate ligand (the quinoline nitrogen) by the oxygen of a perchlorate ion. Usually, the solid-state structure of a species cannot be considered as a warranty of its solution behavior. However, in this case the displacement of a nitrogen terminus must be definitely promoted by the rearrangement of the complex itself in solution. Furthermore, the lack of diastereotopicity of the CH₂S protons indicates that the rate of sulfur absolute configuration inversion is fast with respect to the NMR time scale. The NNN(Qui) derivatives behave very similarly to those of the NSN ligand. Also in these cases no coupling between Hg, Cd, and protons is observed, the aromatic protons H² and H^{2'} resonate at higher field with respect to the free ligand in both the complexes; no diastereotopicity was observed for CH₂N protons which, however, resonate at field values very similar to those of the free ligand. The complexes [Zn(LL'L')₂](ClO₄)₂ [LL'L' = NSN(Qui), NNN(Qui)] behave similarly. However, the H² and H^{2'} protons of the complex [Zn[NSN(Qui)]₂](ClO₄)₂ resonate down field with respect to the free ligand, apparently no interference between the ring currents being operative in this case.

The most prominent features of the bis-chelate derivatives of the ligand NNNtos(Qui) are the diastereotopicity of the CH₂N protons and the signals due to the H² and H^{2'} protons which resonate downfield with respect to the free ligand. The tosyl group in planar tetra-coordinated complexes was shown to lie almost perpendicular to the main complex coordination plane thereby inducing an asymmetry in the sp³ CH₂N protons which give rise to an AB system when the rearrangement movement is slow in the NMR time scale.^[12] All the ¹H NMR spectra of complexes [M{NNNtos(Qui)}₂](ClO₄)₂ (M = Hg, Cd, Zn) display for the CH₂N protons an AB system indicating a slow rearrangement of the tosyl wing around the metal center. The down-field resonance of the aromatic H² and H^{2'} protons is also detected in the case of Hg and Cd complexes with NNNtos(Qui) but, probably because of the compensating effect of the tosyl fragment which is orthogonal to the complex main plane, no interactions between ring currents are observable.

Moreover, in the cases of the Hg and Cd derivatives, the ¹H NMR low-temperature spectra display the ¹⁹⁹Hg¹H and ^{111/113}Cd¹H coupling for the signals due to the CH₂N and H² and H^{2'} protons.

Monochelate Dichloro Complexes

Addition of the ligand $LL'L''$ [$LL'L'' = NSN(Qui)$, $NNN(Qui)$, $NNNtos(Qui)$] to MCl_2 ($M = Hg, Cd, Zn$) in methanol yields the corresponding monochelate dichloro complexes of general formula $[M(LL'L'')Cl_2]$. In any case a general down-field shift of the ligand signals of the CH_2S , CH_2N , and aromatic protons is observed upon coordination. The CH_2N shift for both the NNN ligands is less pronounced being almost isochronous with that of the free ligand. The lack of a high-field shift of the H^2 and $H^{2'}$ aromatic protons induced by the currents of the opposite rings represents a useful clue to monochelation.

X-ray Crystal Structure

The ORTEP^[15] representations of the complexes $[Hg\{NSN(Qui)\}Cl_2]$ (**1**), $[Hg\{NSN(Qui)\}_2(OCIO_3)](ClO_4)$ (**2**), and $[Zn\{NNN(Qui)\}Cl_2]$ (**3**) together with the employed numbering schemes are shown in Figures 1, 2, and 3, respectively. Complexes **1** and **3** are neutral and five-coordinate; complex **2** is cationic and six-coordinate.

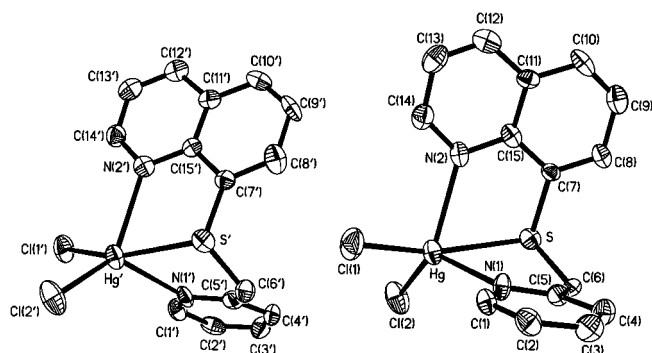


Figure 1. Anisotropic ellipsoid representation of the *TBPY-5-12-C* (right) and *TBPY-5-12-A* (left) units of complex **1**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted.

Five-coordinate complexes 1 and 3: In complexes **1** and **3** the environment of the metal is given by a tridentate [$NSN(Qui)$ or $NNN(Qui)$] ligand and by two chloride ions. Notably, in the unit cell of **1** there are two crystallographically independent complexes that are mirror images without forming, however, an enantiomeric pair (see below). The coordination geometry of both units appears intermediate between square pyramidal (*sp*) and trigonal bipyramidal (*tbp*), while it is square pyramidal in **3**. The τ angular structural index^[16] (ideal values: 0 for *sp* and 1 for *tbp* geometry) was used to measure the deviation from either one of the ideal arrangements in **1** and **3**. In the two units of **1** $\tau = 0.59$ and $\tau = 0.45$ (average 0.52), whereas $\tau = 0.01$ in **3**. Accordingly, we considered the two units of **1** like distorted *tbp* complexes. In this description, the apical positions around Hg are taken by the Cl(1) chloride and by the S atom of the chelate ligand, while the equatorial plane is filled by the Cl(2), N(1), and N(2) atoms. In **3**, the Cl(1) chloride takes the apical position above Zn and the basal plane is filled by the Cl(2), N(1), N(2), and N(3) atoms.

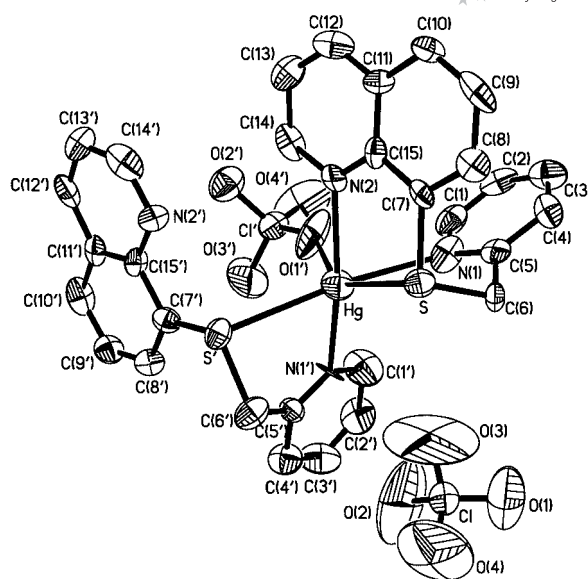


Figure 2. Anisotropic ellipsoid representation of complex **2**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted.

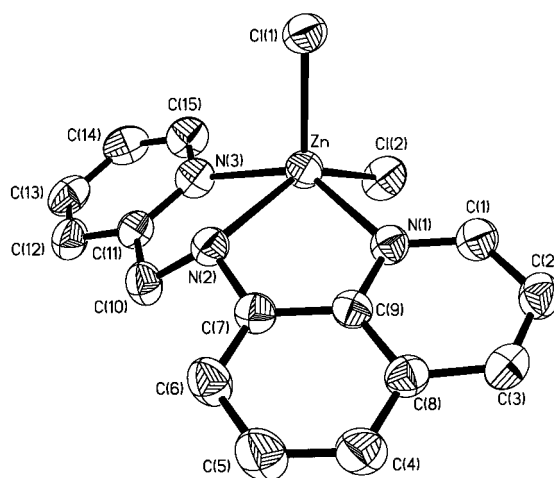


Figure 3. Anisotropic ellipsoid representation of complex **3**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted.

For the sake of clarity, in the remaining part of the discussion the two units of **1** will be named *TBPY-5-12-C* and *TBPY-5-12-A*, following the IUPAC^[17] recommendations for determining the absolute configuration in inorganic compounds and the CIP (Cahn, Ingold, and Prelog) priority rules.^[18] As noticed above, the two units are not alike and the difference becomes clear by comparing the angles Cl(1)–Hg–S, N(1)–Hg–N(2) (imposed by chelation), N(1)–Hg–Cl(1), N(2)–Hg–Cl(1), and S–Hg–Cl(2), whose values are 163.1(1), 95.2(3), 97.5(3), 94.6(3), and 90.8(1)° in *TBPY-5-12-C* and 156.5(1), 97.2(4), 93.8(3), 89.4(3), and 97.1(1)° in *TBPY-5-12-A*, respectively. The Hg atom also deviates from the equatorial plane by 0.42 Å in *TBPY-5-12-C* and 0.31 Å in *TBPY-5-12-A*. In **3**, the departure of the Zn atom

from the basal plane is even larger (0.66 Å) and such deviation implies that all the Cl(1)–Zn–equatorial donor angles are well above 90° (from 104.8 to 111.9°).

Our findings were compared with data taken from the Cambridge Crystallographic Database (CCD).^[19] We searched the repository looking for (a) five-coordinate monomeric Hg^{II} complexes containing a thioether ligand, (b) five-coordinate monomeric Hg^{II} complexes containing at least two pyridine-like ligands, (c) five-coordinate Zn^{II} complexes containing at least two pyridine-like ligands and an N₃Cl₂ coordination set. Search (a) returned nine entries. In these structures, the Hg^{II}–S(thioether) distances vary from 2.491^[20] to 2.822^[21] Å. The values found in *TBPY-5-12-C* and *TBPY-5-12-A* [2.759(4) and 2.748(3) Å, respectively] fit in the range and are close to those of the cations described in the literature^[21,22] (2.731 and 2.727 Å, respectively).

Search (b) yielded 13 entries, in which the reported Hg^{II}–N(pyridyl) distances vary from 2.235^[23] to 2.619^[24] Å. The values found in *TBPY-5-12-C* and *TBPY-5-12-A* are 2.350(9), 2.44(1) Å and 2.38(1), 2.44(1) Å, respectively [the longer Hg^{II}–N bond always involving N(2)], again within the experimental range, and are similar to those found in the cation reported in ref.^[25] (2.363, 2.401 Å) and in the neutral complexes reported in ref.^[26] (2.373, 2.400 Å) and ref.^[27] (2.372, 2.429 Å). The Hg–Cl distances are 2.455(4), 2.450(3) Å in *TBPY-5-12-C* and 2.494(4), 2.428(4) Å in *TBPY-5-12-A*. The longer Hg–Cl bond always involves the Cl(1) *trans* to S. These data agree with CCD values for 35 five-coordinate complexes (2.238–3.029 Å).

It is worth noting that complexes in which a five-coordinate Hg^{II} is surrounded at the same time by pyridyl and thioether ligands are rather uncommon.^[22,25] Recently, Bebout and co-workers^[14] described some zinc triad complexes (with c.n. = 4, 5, or 6) of a symmetric N,S mixed ligand (L) closely related to NSN(Qui). The Hg–N, Hg–S distances found in **1** fit reasonably well with the values quoted by Bebout for six-coordinate Hg^{II} complexes with pyridyl (2.352–2.557 Å) or crown-thioether ligands (2.458–2.751 Å), whereas the Hg–Cl terminal bonds are somewhat longer than those reported for either four-coordinate Hg(L)Cl₂ [2.4049(8), 2.4099(8) Å] or five-coordinate Hg₂(L)Cl₄ [2.336(2), 2.395(2) Å].^[14]

Search (c) returned about 20 entries, but only 11 of these show an aliphatic amine donor atom like **3**. In the reported structures, the Zn–N_{py}, Zn–N_{ali} (N_{py} = pyridine nitrogen, N_{ali} = aliphatic amine nitrogen), and Zn–Cl distances vary, respectively, in the ranges 2.039^[28]–2.511,^[28] 2.129^[29]–2.464,^[30] and 2.220^[30]–2.345^[29] Å. In **3**, the Zn–N_{py} bonds are 2.124(3), 2.156(3) Å, Zn–N_{ali} is 2.234(3) Å, and the Zn–Cl distances are 2.252(1) and 2.343(1) Å, respectively. The longer Zn–Cl bond involving the Cl(2) chloride *trans* to the aliphatic amine N(2) appears to be the second longest reported so far after 2.345 Å in ref.^[29]. An overall arrangement about Zn similar to that of **3** is found in the complexes described in ref.^[31,32] and to a lesser degree in those reported in refs.^[29,33]

The chloride ligands of **1** and **3** are involved in a network of nonbonding interactions, which appears to be more ex-

tended in **1**. The intermolecular contacts are listed in detail in Table 2SI of the Supporting Information. The packing diagram of **1** also reveals that the quinoline rings of adjacent molecules are stacked in the solid state. The stacking occurs along the crystallographic *a* axis, in a head-to-tail arrangement. The separation between the planes is 3.47 Å as compared to 3.40 Å in graphite.

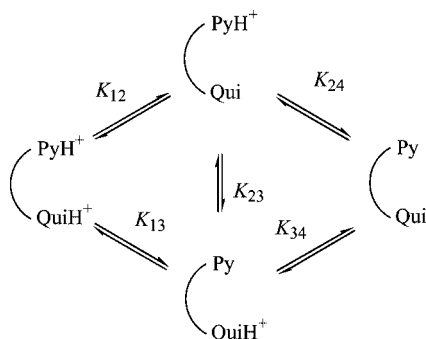
Six-coordinate complex **2**: In this cation (Figure 2) one of the two NSN(Qui) donors acts as tridentate and the other one as bidentate. The coordination position that is not occupied by the quinolyl N atom is taken by a perchlorate anion. This situation is unusual, and to the best of our knowledge, in the CCD there is no structure of general formula [M(LL'L)₂] (M = six-coordinate metal, L, L' = N, S or O, LL'L = tridentate ligand forming with the metal two adjacent five-membered rings) showing a similar arrangement. The uncommon coordinating behavior shown by one NSN donor might be due, at the first glance, to somewhat greater steric demand of the perchlorate anion, compared to the chloride one in **1**. However, we also suspect that the expected [Hg{NSN(Qui)}₂](ClO₄)₂ was represented by the colorless specimen of **2** that we could not characterize by X-ray diffraction (see Experimental Section). We will try to clarify this issue in future investigations.

The coordination environment around Hg is distorted octahedral. The dihedral angle formed by the face N(1), N(2), S with the triangle opposed to it is 30.5° (ideal value = 0°). The base plane is defined by the N(1), N(2), N(1') and S' atoms. The largest deviation from this plane is shown by N(1') (–0.15 Å), while Hg itself deviates by +0.20 Å. The severe distortion of the octahedron is mainly due to the narrow S–Hg–O(1') angle [144.1(3)°] and to the variability in Hg–N distances. In fact, in the tridentate NSN(Qui) Hg–N(1) 2.63(1) Å, Hg–N(2) 2.28(1) Å, while in the bidentate NSN(Qui) Hg–N(1') 2.23(1) Å. Likewise, in the tridentate donor, the Hg–S–C(6) and Hg–S–C(7) angles are 97.1 and 96.1°, respectively, while the Hg–S'–C(6') and Hg–S'–C(7') angles in the bidentate unit are 87.7 and 113.1°, respectively.

A comparison with existing data was made searching the CCD repository for (a) six-coordinate monomeric Hg^{II} complexes containing a thioether ligand, (b) six-coordinate monomeric Hg^{II} complexes with the metal surrounded by at least four pyridyl ligands. Search (a) returned ten entries, in which the Hg^{II}–S(thioether) distance varies between 2.458^[34] and 3.050^[34] Å. In **2**, there is a shorter and a longer Hg–S bond [2.621(4) Å and 2.749(5) Å], a situation already found by Bebout^[14] [bonds of 2.654(1) and 2.671(1) Å] and also quite similar to what was observed in the complexes described in ref.^[35] (bonds of 2.654, 2.735, 2.639, 2.751 Å) and ref.^[36] (distances of 2.728, 2.638, and 2.712 Å).

Search (b) returned eight entries, with Hg^{II}–N(pyridyl) distances ranging from 2.271^[37] to 2.685^[38] Å. The shorter and longer Hg–N distances found in **2** [2.23(1), 2.28(1), 2.63(1) Å] again fit into the experimental range, with the shorter bond being in fact the shortest Hg–N(pyridyl) bond so far reported, about 0.04 Å shorter than the one reported

in ref.^[37] (2.271 Å), and the longer one being the second longest after the one found in ref.^[38] (2.685 Å). A similar situation with shorter and longer Hg–N distances has been reported by Bebout^[14] [2.382(4), 2.409(4) Å, 2.501(4), 2.511(4) Å] as well as in the cation described in ref.^[39] (2.351, 2.418, 2.413 Å). Taken all together, these data suggest that the asymmetry of the ligand and the steric requirements of the quinolyl moiety are responsible for the NSN(Qui) donor failing to bind mercury in a bis-tridentate fashion as well as for the variation in the Hg–S, Hg–N bond lengths (Scheme 2).



Scheme 2.

It is also worth noting that the perchlorate ligand is rather unusual in Hg^{II} complexes. A search in the CCD returned only five structures, in which the Hg–O distance ranges between 2.569 and 2.932 Å. The only six-coordinate Hg complex reported^[13] shows Hg–O distances of 2.569 and 2.650 Å, comparing well with our value of 2.60(1) Å. Like in **1** above, the oxygen atoms of the two perchlorate residues and the quinolyl N atom of the bidentate NSN(Qui) donor are involved in a network of nonbonding interactions. The intermolecular contacts are detailed in Table 2SI.

Determination of the Acid Dissociation Constants

The determination of the acid dissociation constants of the ligands was performed by potentiometric titration with NaOH (0.1 M) of the conjugated acids of the ligand

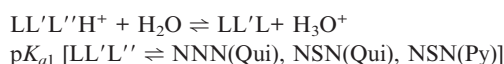
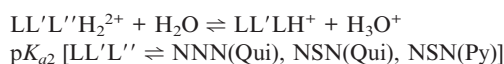
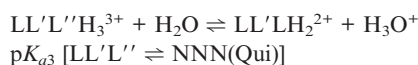
Table 1. Macroconstant set determined by titration with NaOH (0.1 M) of the acid LL'L''*n*HCl (*n* = 2, 3) in degassed water (*I* = 0.1) at 25 °C.

LL'L'' <i>n</i> HCl	p <i>K</i> _{a3}	p <i>K</i> _{a2}	p <i>K</i> _{a1}
NSN(Py)·2HCl	/	3.33 ± 0.04	5.23 ± 0.02
NSN(Qui)·2HCl	/	2.98 ± 0.14	4.83 ± 0.03
NNN(Qui)·3HCl	<2	2.80 ± 0.13	4.84 ± 0.02

Table 2. Microconstant set determined by titration with NaOH (0.1 M) of the acid LL'L''*n*HCl (*n* = 2, 3).

In degassed water (<i>I</i> = 0.1) at 25 °C	p <i>K</i> ₁₂	p <i>K</i> ₁₃	p <i>K</i> ₂₄	p <i>K</i> ₃₄	p <i>K</i> ₂₃
NSN(Py)·2HCl	3.63 ± 0.16	3.63 ± 0.16	4.93 ± 0.02	4.93 ± 0.02	0.00 ± 0.03
NSN(Qui)·2HCl	3.09 ± 0.02	3.63 ± 0.04	4.72 ± 0.19	4.18 ± 0.21	0.54 ± 0.06
NNN(Qui)·3HCl	2.87 ± 0.02	3.63 ± 0.04	4.77 ± 0.17	4.01 ± 0.19	0.76 ± 0.06

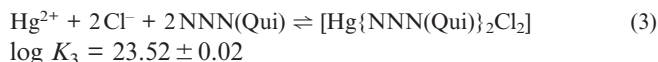
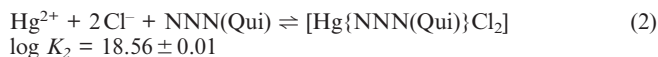
[NNN(Qui)·3HCl; NSN(Qui)·2HCl; NSN(Py)·2HCl] produced in situ by addition of the stoichiometric amount of HCl (0.1 M) in degassed water at controlled ionic strength (0.1 M, NaCl) under N₂ stream. The pH vs. titrant volume data were elaborated by means of routines appropriately written in the SCIENTISTTM environment. The macroconstant and microconstant sets are referred for each ligands to the following general schemes and are reported in Tables 1 and 2, respectively (see Supporting Information).



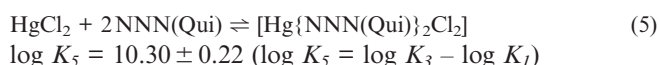
Determination of the Formation Equilibrium Constants

Hg

The spectrophotometric titration of the ligand NNN(Qui) with HgCl₂ was performed in water and resolved by means of the HYPERQUADTM 2003 program^[40] according to the model:



It is apparent that the formation of the species in solution is influenced by the ligand/Hg ratio and by the equilibrium constants, equilibrium (3) being the most favored at high NNN(Qui)/Hg ratios. The formulation of the complex [Hg{NNN(Qui)}₂Cl₂] does not imply any structural preference since several attempts to produce crystals suitable for X-ray collection were unsuccessful and a mixture of uncharacterized products was always obtained. According to the structure of [Hg{NSN(Qui)}₂(OCIO₃)](ClO₄) (**2**) and to the chloride coordinating characteristics, we suggest that this species could be represented as a neutral six-coordinate octahedral complex bearing two partially coordinated NNN(Qui) fragments and two chlorides. The pH of the unbuffered solution hardly deviates from 6.5 and therefore no protonation equilibrium of the ligand occurs (see Supporting Information) and no formation of mercury hydroxide is observed. Moreover, owing to the stability of the HgCl₂ species the equilibrium constants are better described as shown in equations 4 and 5.



As a matter of fact the complex $[\text{Hg}\{\text{NNN(Qui)}\}\text{Cl}_2]$ in solution dissociates according to step (4) but at variance with zinc (vide infra) the dissociation constant (ca. 6×10^{-6}) is badly determined owing to the unfavorable change of absorbance as a function of concentration.

The equilibrium constants between mercury and the NSN ligands were also determined in a similar way and a summary of the results is reported in the following Table 3.

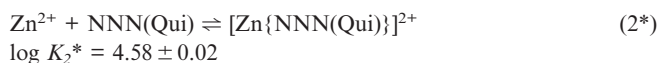
Table 3. Log K_2 , log K_3 , log K_4 , and log K_5 for the reaction of HgCl_2 with terdentate NNN or NSN ligands in H_2O at 25 °C.

Ligand	log K_2	log K_3	log K_4	log K_5
NNN(Qui)	18.56 ± 0.01	23.52 ± 0.02	5.34 ± 0.21	10.30 ± 0.22
NSN(Qui)	18.84 ± 0.04	23.52 ± 0.04	5.62 ± 0.24	10.30 ± 0.24
NSN(Py)	18.60 ± 0.07	22.95 ± 0.13	5.38 ± 0.27	9.73 ± 0.33

As can be seen the equilibrium constant values are hardly influenced by the nature of the chelating ligands. However, only some complexes of the ligands NNNtos(Qui) and NNN(Qui) display fluorescence activity, the latter being the more soluble species; for this reason we decided to extend our investigation on zinc and cadmium using NNN(Qui) as the complexing agent.

Zn

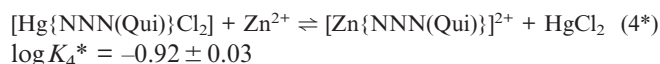
Analogously to the Hg case the values of the equilibrium constants were determined by direct titration of a ca. 1×10^{-4} mol dm⁻³ solution of the ligand NNN(Qui) with ZnCl_2 . The model fitted by means of the HYPERQUADTM 2003 program^[40] was as shown in equations 1* to 3*.



As can be seen, chloride does not compete efficiently with oxygenated ligands (H_2O), thus the zinc complexes were written with vacant coordination sites which might be occupied by H_2O , Cl^- , and OH^- , the latter being the less probable since $\text{p}K_a \text{Zn}(\text{H}_2\text{O})_x^{2+} \approx 9$.

At variance with mercury, reaction 2* can be checked by studying the dissociation of the complex $[\text{Zn}\{\text{NNN(Qui)}\}]^{2+}$ taking place upon dilution. In this case the favorable absorbance change allows the determination of $1/K_2^* = 1 \times 10^{-5}$ (log $K_2^* = 5 \pm 0.5$) which is in substantial agreement with the value of log $K_2^* = 4.58$ previously determined.

Moreover, it is possible to study the direct exchange between the Hg complex and $\text{Zn}(\text{ClO}_4)_2$ according to the reaction 4*.



From reactions 4 and 4* the value of log $K_2^* = 4.42 \pm 0.24$ is obtained.

It is apparent that an internal consistency among the K_2^* values is achieved. Thus, according to the previous choice the value of log $K_2^* = 4.58 \pm 0.02$ is assumed.

Cd

The direct exchange between the species $[\text{Zn}\{\text{NNN(Qui)}\}]^{2+}$ and Cd^{2+} according to the model described below. Reaction 1** can be treated as a combination of 2* and 3**.



In this respect from the titration of a dechlorinated solution of $[\text{Zn}\{\text{NNN(Qui)}\}]^{2+}$ (from $[\text{Zn}(\text{NNN(Qui)})\text{Cl}_2]$ treated with AgClO_4) with $\text{Cd}(\text{ClO}_4)_2$ it is possible to obtain the logarithm of the formation constant K_3^{**} as the refined parameter, the formation constant for zinc K_2^* being held constant (4.58 ± 0.02) throughout the fitting process. The chloride ions were removed from the solution in order to avoid formation of cadmium complexes containing chloride bridges which might complicate the resolution of the system. Moreover, no precipitation problems arise under these conditions.

As an internal check of consistency the direct titration of Cd^{2+} ($\text{Cd}(\text{ClO}_4)_2$) with NNN(Qui) ligand was also performed and the value of 2.89 ± 0.01 for log K_3^{**} was determined by means of the customary HYPERQUADTM 2003 program.^[40] In the presence of an excess of NNN(Qui) ligand a further equilibrium takes place.



The independently determined values for K_3^{**} are in good agreement with each other, this fact confirming the model reliability and the consistency of the different approaches.

The equilibrium constants measured in the cases of Zn^{2+} and Cd^{2+} complexes lie among the values reported in the literature when di(2-pyridyl)amine and bis[(2-pyridyl)methyl]amine are used as ligands.^[42] The case of Hg^{2+} complexes turns out to be more difficult to compare since the data in the literature are referred to complexes without chloride. The log K_3 value (23.52 ± 0.02), however, is in substantial agreement with that found by other authors when $\text{Hg}(\text{NO}_3)_2$ is reacting with bis[(2-pyridyl)methyl]amine.^[42] In this respect it is noteworthy that the ionic strength control in the titration of the ligand with HgCl_2 is irrelevant since only neutral molecules are involved.

The titration spectra and the values of the extinction coefficients are reported in the Supporting Information (Table 3SI).

Spectroscopic Properties of the Ligands

The spectral features of the ligands NNN(Qui) and NSN(Qui) in different solvents are summarized in Table 4.

Table 4. Absorption and emission ($\lambda_{\text{exc}} = 320$ nm) maxima and fluorescence quantum yields of the ligands NNN(Qui) and NSN(Qui) in different solvents.

Ligand	Solvent	λ_{abs} [nm]	λ_{em} [nm]	Φ
NNN(Qui)	<i>n</i> -hexane	260	426	<0.001
		365		
	CH ₃ CN	258	489	0.020 ± 0.002
		360		
H ₂ O	252	–	–	
	337			
NSN(Qui)	<i>n</i> -hexane	253	380	0.010 ± 0.001
		340		
	CH ₃ CN	251	420	0.020 ± 0.002
		332		
	H ₂ O	248	453	0.10 ± 0.01
		317		

The most prominent spectral changes observed at increasing solvent polarity for both ligands are the following: *i*) a marked blue shift of the first $\pi\pi^*$ absorption band, *ii*) a red shift of the fluorescence emission with a concomitant increase of the Stokes shift, and *iii*) an increase of fluorescence quantum yields. These changes are consistent with a stabilization of both the ground and the first excited singlet state by polar solvents.^[43] NNN(Qui) is fluorimetrically silent in H₂O; this could be attributed to the occurrence of a bimolecular quenching induced by the formation of an H-bond with the central amine nitrogen.

The water-insoluble NNNtos(Qui) does not show any fluorescence signal in organic solvents, probably because of an intramolecular quenching due to rotation of the tosyl moiety around the N–S bond.

Fluorescence Properties of the Complexes

Both the complexes [Zn{NNN(Qui)}Cl₂] and [Zn{NNNtos(Qui)}Cl₂] are soluble and fluorescent in H₂O. Probably, metal coordination to the aliphatic nitrogen in [Zn{NNN(Qui)}Cl₂] prevents its interaction with the protic solvent;^[44] the fluorescence quantum yield, however, is very low ($\Phi < 0.001$). On the contrary, a relatively high quantum yield Φ is observed for [Zn{NNNtos(Qui)}Cl₂], both in H₂O [$\lambda_{\text{em}}^{\text{max}}$ (nm) = 440; $\Phi = 0.050 \pm 0.005$] and CH₃CN [$\lambda_{\text{em}}^{\text{max}}$ (nm) = 375; $\Phi = 0.020 \pm 0.002$]. A plausible explanation for this behavior is that steric constraint due to metal–N chelation limits the rotational freedom of the tosyl group, thereby preventing the fluorescence quenching observed for the free ligand.

The fluorescent behavior of the ligand NNN(Qui) has also been studied with Cd²⁺. A mild increase (twofold) of

the fluorescent signal at $\lambda_{\text{em}} = 520$ nm has been observed for a Cd/NNN(Qui) ratio of 2000/1. This is probably due to the high spin/orbit coupling constant of Cd²⁺. For the sake of completeness a Table summarizing the photochemical properties of several complexes bearing similar ligands and the related references is reported in the Supporting Information (Table 4SI).

Conclusions

From the present study it may be deduced that:

a) Bis-chelate complexes of the zinc triad with terdentate and potentially fluorescent ligands of the type NNN or NSN are easily obtained when perchlorate salts of the metals are used in the coordination reaction.

b) Monochelate complexes of the zinc triad with the above-mentioned ligands are easily obtained when chloride salts of the metals are used.

c) Among the X-ray determinations the structure of the complex [Hg{NSN(Qui)}OClO₃]ClO₄, which is quite unusual, bears witness to the flexibility in solution of this sort of ligand when coordinated to d¹⁰ metals.

d) The macroscopic and microscopic set of acid dissociation constants for the terdentate NSN and NNN ligands has been determined.

e) The fluorescence of the ligands and of the corresponding metal complexes has been studied. In the case of the fluorescent silent ligands NNN(Qui) and NNNtos(Qui) the corresponding complexes with Zn were shown to be fluorescent.

Experimental Section

Solvents and Reagents: CH₃CN, CH₃OH, and H₂SO₄ were commercial-grade chemicals and were used without further purification. HCl (0.1 M) and NaOH (0.1 M) were prepared by appropriate dilution of NORMEX solutions (Carlo Erba Reagents). Hg(ClO₄)₂·6H₂O, Cd(ClO₄)₂·6H₂O (Alfa-Aesar), Zn(ClO₄)₂·6H₂O, AgNO₃, HgCl₂, CdCl₂·H₂O, ZnCl₂ (Sigma–Aldrich), and CD₃CN and CD₃OD were commercial-grade reagents and used without further purification.

IR, NMR, UV/Vis, and Fluorescence Measurements: IR and ¹H and ¹³C{¹H} NMR spectra were recorded with a Perkin–Elmer Spectrum One spectrophotometer and a Bruker Avance 300 spectrometer, respectively. The proton and carbon assignment was performed by ¹H–¹³C-HMQC and HMBC techniques in the case of the bis-chelate complexes [ML₂](ClO₄)₂ [M = Zn, Cd, Hg; L = NSN(Qui), NNN(Qui)]. The proton assignment for the chlorinated complexes [MLCl₂] [M = Zn, Cd, Hg; L = NSN(Qui), NNN(Qui)] and for all complexes with NNNtos(Qui) as ancillary ligand was achieved by ¹H–¹H-COSY experiment because of their low solubility. UV/Vis spectra were taken with a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier temperature programmer) apparatus. All fluorescence spectra were recorded with a Perkin–Elmer luminescence spectrometer LS 50 (*T* = 298 K) and fluorescence quantum yields Φ_{X} were measured relative to quinine sulfate in H₂SO₄ (0.5 M) as a standard and calculated according to the following formula:

$$\Phi_X = \Phi_{ST} \frac{S_X}{S_{ST}} \cdot \frac{A_{ST}}{A_X} \cdot \frac{n_X^2}{n_{ST}^2}$$

where S represents the area of the corrected emission fluorescence spectra ($\lambda_{\text{exc}} = 320$ nm), A is the optical density at 320 nm, and n the refractive index of the solvent used.

Synthesis of Ligands: The synthesis of the ligands NSN(Py), NSN(Qui), and NNNtos(Qui) was carried out according to the published procedure.^[12]

8-[(Pyridylmethyl)amino]-quinoline NNN(Qui): To concentrated H_2SO_4 (7.5 mL) 8-*N*-tosyl-*N*-(2-pyridylmethyl)quinoline [NNNtos(Qui)] (2.358 g, 6.05 mmol) was added and the solution was stirred for 2 h at 110 °C. To the resulting mixture a saturated aqueous solution of NaCl (10 mL) and NaOH (6 M, 60 mL) was added. The neutral residue was extracted with CH_2Cl_2 and washed with a saturated aqueous solution of NaCl. The organic phase was eventually dried under vacuum. The crude product was purified by flash chromatography through a silica column with a 1:1 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture as eluent. Concentration under vacuum of the eluate yields 1.088 g (4.62 mmol) of the title compound as a yellow/green oil. Yield 76%. ^1H NMR (CD_3CN , $T = 298$ K): δ = aminomethyl protons, 4.66 (d, $J_{\text{CH}_2\text{-NH}} = 5.92$ Hz, 2 H, pyr- CH_2N), amine protons 7.25 (br. s, 1 H, pyr-NH), pyridine and quinoline protons 6.67 (dd, 1 H, 7- H_{qui}), 7.11 (dd, $J = 7.93$ Hz and $J = 1.15$ Hz, 1 H, 5- H_{qui}), 7.27 (dd, $J = 4.83$ Hz, 1 H, 3'- H_{pyr}), 7.36 (t, 1 H, 6- H_{qui}), 7.41 (d, 1 H, 5'- H_{pyr}), 7.48 (dd, 1 H, 3- H_{qui}), 7.72 (td, $J = 8.00$ and $J = 1.75$ Hz, 1 H, 4'- H_{pyr}), 8.18 (dd, $J = 8.33$ and $J = 1.75$ Hz, 1 H, 4- H_{qui}), 8.62 (d, 1 H, 2'- H_{pyr}), 8.79 (dd, $J = 4.17$ Hz, 1 H, 2- H_{qui}) ppm. ^{13}C NMR (CD_3CN , $T = 298$ K): δ = thiomethyl carbon, 48.03 (pyr- CH_2N), pyridine C atoms 121.34, 121.59, 122.04 (C-5'- pyr , C-3'- pyr , C-3- qui), 136.54 (C-4'- pyr), 149.00 (C-2'- pyr), 158.50 (C-6'- pyr), quinoline C atoms 104.91 (C-5- qui), 113.90 (C-7- qui), 127.63 (C-6- qui), 128.56 (C-4a- qui), 138.05 (C-8- qui), 138.83 (C-4- qui), 144.36 (C-8a- qui), 147.14 (C-2- qui) ppm. ^1H NMR (CDCl_3 , $T = 298$ K): δ = aminomethyl protons, 4.73 (d, $J = 5.8$ Hz, 2 H, pyr- CH_2N), amine protons 7.03 (br. s, 1 H, pyr-NH), pyridine and quinoline protons 7.09 (dd, $J = 8.1$ and 1.1 Hz, 1 H, 5- H_{qui}), 7.20 (dd, $J = 4.7$ and 7.6 Hz, 2 H, 3'- H_{pyr}), 7.34 (t, $J = 7.5$ Hz, 1 H, 6- H_{qui}), 7.41 (m, 2 H, 3- H_{qui} , 5'- H_{pyr}), 7.63 (td, $J = 7.6$ and 1.8 Hz, 1 H, 4'- H_{pyr}), 8.09 (dd, $J = 8.3$ and 1.7 Hz, 1 H, 4- H_{qui}), 8.65 (d, 1 H, 2'- H_{pyr}), 8.79 (dd, $J = 4.2$ Hz, 1 H, 2- H_{qui}) ppm. ^{13}C NMR (CDCl_3 , $T = 298$ K): δ = thiomethyl carbon, 49.1 (pyr- CH_2N), pyridine C atoms 121.0, 121.4, 121.9 (C-5'- pyr , C-3'- pyr , C-3- qui), 136.6 (C-4'- pyr), 149.3 (C-2'- pyr), 158.9 (C-6'- pyr), quinoline C atoms 105.2 (C-5- qui), 114.3 (C-7- qui), 127.6 (C-6- qui), 128.6 (C-10- qui), 138.3 (C-4- qui), 144.3 (C-9- qui), 147.0 (C-2- qui) ppm.

Synthesis of Bis-Chelate Complexes

[Hg{NNN(Qui)}₂](ClO₄)₂: A solution of $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0861 g, 0.18 mmol) in acetonitrile (4 mL) was added slowly to a stirred solution of NNN(Qui) (0.09 g, 0.38 mmol) in acetonitrile (2 mL). The resulting solution was diluted 1:1 with toluene at 0 °C. The solution was concentrated under reduced pressure and the complex precipitated. The complex was filtered off, washed with toluene, pentane, and dried under vacuum. Cream microcrystals were obtained (0.1224 g, 0.14 mmol). Yield 80%. IR (KBr): $\tilde{\nu} = \nu_{\text{N-H}} 3289.4$, $\nu_{\text{C-H}} 3048.0$, 2920.7, $\nu_{\text{C=N}} 1613.4$, $\nu_{\text{C=C}} 1512.8$, 1445.8, $\nu_{\text{ClO}_4^-} 1090.5$ cm^{-1} . ^1H NMR (CD_3CN , $T = 298$ K): δ = aminomethyl protons, 4.69 (s, 4 H, pyr- N-CH_2), amine protons, 6.14 (br. s, 2 H, pyr-NH), pyridine and quinoline protons 7.39 (d, $J = 8.2$ and 4.5 Hz, 2 H, 3- H_{qui}), 7.58 (m, 6 H, 6- H_{qui} , 7- H_{qui} , 3'- H_{pyr}), 7.69 (dd, $J = 7.35$ and 2.3 Hz, 2 H, 5- H_{qui}), 7.75 (d, $J = 7.9$ Hz, 2

H, 5'- H_{pyr}), 8.14 (td, $J = 7.7$ and 1.7 Hz, 2 H, 4'- H_{pyr}), 8.25 (m, 4 H, 4- H_{qui} , 2- H_{qui}), 8.42 (d, $J = 4.8$ Hz, 2 H, 2'- H_{pyr}) ppm. ^{13}C NMR (CD_3CN , $T = 298$ K): δ = aminomethyl C atoms, 51.7 (pyr- N-CH_2), quinoline C atoms 122.0 (C-3- qui), 125.2, 125.8 (C-5- qui , C-7- qui), 127.39 (C-6- qui), 128.2 (C-8- qui), 128.8 (C-10- qui), 138.9 (C-4- qui), 139.0 (C-9- qui), 150.3 (C-2- qui); pyridine C atoms 122.4 (C-3'- pyr), 125.8 (C-5'- pyr), 141.2 (C-4'- pyr), 149.1 (C-2'- pyr), 154.6 (C-6'- pyr) ppm. $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{HgN}_6\text{O}_8$: calcd. C 41.41, H 3.01, N 9.66; found C 41.25, H 2.97, N 9.51.

The following complexes were synthesized in an analogous way using the appropriate perchlorate salts.

[Cd{NNN(Qui)}₂](ClO₄)₂: Yield 85% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{\text{N-H}} 3251.4$, $\nu_{\text{C-H}} 3078.6$, 2931.4, $\nu_{\text{C=N}} 1613.3$, $\nu_{\text{C=C}} 1511.0$, 1440.6, $\nu_{\text{ClO}_4^-} 1107.9$ cm^{-1} . ^1H NMR (CD_3CN , $T = 298$ K): δ = aminomethyl protons, 4.61 (s, 4 H, pyr- N-CH_2), amine protons, 5.70 (br. s, 2 H, pyr-NH), pyridine and quinoline protons 7.48 (m, 4 H, 3- H_{qui} , 3'- H_{pyr}), 7.65 (d, $J = 7.7$ Hz, 2 H, 5'- H_{pyr}), 7.72 (t, 2 H, 6- H_{qui}), 7.85 (dd, $J = 6.2$ Hz, 2 H, 7- H_{qui}), 7.90 (dd, $J = 8.3$ and 1.1 Hz, 2 H, 5- H_{qui}), 8.08 (td, $J = 7.7$ Hz, 2 H, 4'- H_{pyr}), 8.20 (dd, $J = 4.6$ Hz, 2 H, 4- H_{qui}), 8.28 (d, $J = 4.7$ Hz, 2 H, 2'- H_{pyr}), 8.45 (dd, $J = 8.3$ and 1.6 Hz, 2 H, 2- H_{qui}) ppm. ^{13}C NMR (CD_3CN , $T = 298$ K): δ = aminomethyl C atoms, 53.9 (pyr- N-CH_2), quinoline C atoms 122.6 (C-3- qui), 124.9 (C-7- qui), 126.4 (C-5- qui), 127.7 (C-6- qui), 129.2 (C-10- qui), 139.6 (C-2- qui), 139.7 (C-8- qui), 140.5 (C-9- qui), 150.3 (C-4- qui); pyridine C atoms 124.7 (C-5'- pyr), 125.0 (C-3'- pyr), 140.6 (C-4'- pyr), 148.5 (C-2'- pyr), 155.8 (C-6'- pyr). $\text{C}_{30}\text{H}_{26}\text{CdCl}_2\text{N}_6\text{O}_8$: calcd. C 46.08, H 3.35, N 10.75; found C 46.15, H 3.28, N 10.62.

[Zn{NNN(Qui)}₂](ClO₄)₂: The precipitation of the complex was induced by addition of toluene to the reaction mixture. Yield 94% (pale yellow microcrystals). IR (KBr): $\tilde{\nu} = \nu_{\text{N-H}} 3238.6$, $\nu_{\text{C-H}} 3085.0$, 2937.8, $\nu_{\text{C=N}} 1619.7$, $\nu_{\text{C=C}} 1517.4$, 1440.6, $\nu_{\text{ClO}_4^-} 1101.5$ cm^{-1} . ^1H NMR (CD_3CN , $T = 298$ K): δ = aminomethyl protons, 4.70 (s, 4 H, pyr- N-CH_2), amine protons, 6.01 (br. s, 2 H, pyr-NH), pyridine and quinoline protons 7.52 (m, 6 H, 3- H_{qui} , 3'- H_{pyr} , 5'- H_{pyr}), 7.69 (t, 2 H, 6- H_{qui}), 7.81 (br. d, $J = 8.1$ Hz, 2 H, 7- H_{qui}), 7.85 (br. d, $J = 8.4$ Hz, 2 H, 5- H_{qui}), 8.00 (td, $J = 7.8$ and 1.7 Hz, 2 H, 4'- H_{pyr}), 8.43 (d, $J = 8.4$ Hz, 2 H, 4- H_{qui}), 8.49 (br. d, $J = 3.7$ Hz, 2 H, 2'- H_{pyr}), 8.45 (br. d, $J = 5.1$ Hz, 2 H, 2- H_{qui}) ppm. ^{13}C NMR (CD_3CN , $T = 298$ K): δ = aminomethyl C atoms, 53.9 (pyr- N-CH_2), quinoline C atoms 122.6 (C-3- qui), 125.9 (C-7- qui), 126.9 (C-5- qui), 128.0 (C-6- qui), 129.0 (C-10- qui), 139.6 (C-4- qui), 139.6 (C-8- qui), 140.6 (C-9- qui), 149.5 (C-2- qui); pyridine C atoms 124.9, 125.0 (C-5'- pyr , C-3'- pyr), 140.8 (C-4'- pyr), 147.7 (C-2'- pyr), 155.2 (C-6'- pyr) ppm. $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{N}_6\text{O}_8\text{Zn}$: calcd. C 49.03, H 3.57, N 11.44; found C 48.98, H 3.67, N 11.61.

[Hg{NSN(Qui)}₂](ClO₄)₂: A solution (10 mL) of $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.2447 g, 0.5 mmol) in methanol was added slowly to a stirred solution of NSN(Qui) (0.2650 g, 1.05 mmol) in methanol (20 mL). Acetonitrile was then added (30 mL). Volume reduction induces the precipitation of the complex which was filtered off, washed with toluene, *n*-hexane and dried under vacuum. White microcrystals were obtained (0.400 g, 0.44 mmol). Yield 88.5%. IR (KBr): $\tilde{\nu} = \nu_{\text{N-H}} 3251.4$, $\nu_{\text{C-H}} 3078.6$, 2931.4, $\nu_{\text{C=N}} 1613.3$, $\nu_{\text{C=C}} 1511.0$, 1440.6, $\nu_{\text{ClO}_4^-} 1107.9$ cm^{-1} . ^1H NMR (CD_3CN , $T = 298$ K): δ = methylthio protons, 4.77 (s, 4 H, pyr-S- CH_2), pyridine and quinoline protons 7.35 (t, 2 H, 3'- H_{pyr}), 7.46 (d, $J = 7.7$ Hz, 2 H, 5'- H_{pyr}), 7.70 (dd, $J = 4.40$ and 7.7 Hz, 2 H, 3- H_{qui}), 7.86 (m, 4 H, 6- H_{qui} , 4'- H_{pyr}), 8.21 (d, $J = 8.1$ Hz, 2 H, 5- H_{qui}), 8.38 (d, $J = 5.1$ Hz, 2 H, 2'- H_{pyr}), 8.55 (d, $J = 6.6$ Hz, 2 H, 7- H_{qui}), 8.61 (dd, $J = 7.7$ and 1.5 Hz, 2 H, 4- H_{qui}), 8.79 (d, $J = 4.4$ Hz, 2 H, 2- H_{qui}) ppm. ^{13}C NMR (CD_3CN , $T = 298$ K): δ = methylthio C atoms, 42.4 (pyr-S- CH_2), quinoline C atoms 122.9 (C-3- qui), 125.1 (C-10- qui),

128.1 (C-6_{qui}), 130.1 (C-8_{qui}), 132.5 (C-5_{qui}), 139.3 (C-7_{qui}), 141.1 (C-4_{qui}), 142.1 (C-9_{qui}), 152.0 (C-2_{qui}); pyridine C atoms 124.9 (C-3'_{pyr}), 126.9 (C-5'_{pyr}), 140.4 (C-4'_{pyr}), 148.9 (C-2'_{pyr}), 151.4 (C-6'_{pyr}) ppm. C₃₀H₂₄Cl₂HgN₄O₈S₂: calcd. C 39.85; H 2.68, N 6.20; found C 40.02, H 2.67, N 6.41.

The following complexes were synthesized in an analogous way using the appropriate ligand and perchlorate salts.

[Cd{NSN(Qui)}₂](ClO₄)₂: The complex precipitated soon after addition of Cd(ClO₄)₂·6H₂O and no reduction of the volume was necessary. Yield 97% (white microcrystals). IR (KBr): $\tilde{\nu}$ = C-H 3073.7, 2970.8, 2919.3 $\nu_{C=N}$ 1606.6, $\nu_{C=C}$ 1497.4, 1446.0, $\nu_{ClO_4^-}$ 1092.1 cm⁻¹. ¹H NMR (CD₃CN, *T* = 298 K): δ = methylthio protons, 4.74 (s, 4 H, pyr-S-CH₂), pyridine and quinoline protons 7.35 (t, 2 H, 3'-H_{pyr}), 7.53 (d, *J* = 7.7 Hz, 2 H, 5'-H_{pyr}), 7.70 (dd, *J* = 4.7 and 8.3 Hz, 2 H, 3-H_{qui}), 7.88 (m, 4 H, 6-H_{qui}, 4'-H_{pyr}), 8.24 (d, *J* = 8.4 Hz, 2 H, 5-H_{qui}), 8.32 (d, *J* = 5.1 Hz, 2 H, 2'-H_{pyr}), 8.55 (d, *J* = 7.3 Hz, 2 H, 7-H_{qui}), 8.66 (d, *J* = 8.4 Hz, 2 H, 4-H_{qui}), 8.77 (dd, *J* = 4.7 and 1.8 Hz, 2 H, 2-H_{qui}) ppm. ¹³C NMR (CD₃CN, *T* = 298 K): δ = methylthio C atoms, 42.3 (pyr-S-CH₂), quinoline C atoms 122.5 (C-3_{qui}), 125.89 (C-10_{qui}), 128.1 (C-6_{qui}), 130.0 (C-8_{qui}), 130.0 (C-5_{qui}), 139.0 (C-7_{qui}), 140.5 (C-4_{qui}), 143.5 (C-9_{qui}), 152.5 (C-2_{qui}); pyridine C atoms 124.8 (C-3'_{pyr}), 126.4 (C-5'_{pyr}), 140.5 (C-4'_{pyr}), 149.1 (C-2'_{pyr}), 153.0 (C-6'_{pyr}) ppm. C₃₀H₂₄CdCl₂N₄O₈S₂: calcd. C 44.16, H 2.96, N 6.87; found C 44.12, H 2.89, N 6.81.

[Zn{NSN(Qui)}₂](ClO₄)₂: Yield 91% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{C-H} 3072.0, 2993.1, 2933.8, $\nu_{C=N}$ 1604.4, $\nu_{C=C}$ 1505.7, 1485.9, 1446.4, $\nu_{ClO_4^-}$ 1091.0 cm⁻¹. ¹H NMR (CD₃CN, *T* = 298 K): δ = methylthio protons, 4.74 (s, 4 H, pyr-S-CH₂), pyridine and quinoline protons 7.38 (m, 4 H, 3'-H_{pyr}, 5'-H_{pyr}), 7.70 (dd, *J* = 4.8 and 8.4 Hz, 2 H, 3-H_{qui}), 7.81 (td, *J* = 7.7 Hz, 2 H, 4'-H_{pyr}), 7.89 (t, *J* = 7.9 Hz, 2 H, 6-H_{qui}), 8.23 (d, 2 H, 5-H_{qui}), 8.62 (m, 6 H, 2'-H_{pyr}, 4-H_{qui}, 7-H_{qui}), 8.94 (d, *J* = 4.8 Hz, 2 H, 2-H_{qui}) ppm. ¹³C NMR (CD₃CN, *T* = 298 K): δ = methylthio C atoms, 42.6 (pyr-S-CH₂), quinoline C atoms 123.3 (C-3_{qui}), 128.5 (C-6_{qui}), 129.7 (C-8_{qui}), 132.2 (C-5_{qui}), 139.4 (C-7_{qui}), 141.2 (C-4_{qui}), 143.3 (C-9_{qui}), 151.1 (C-2_{qui}); pyridine C atoms 125.1 (C-3'_{pyr}), 126.3 (C-5'_{pyr}), 140.4 (C-4'_{pyr}), 147.4 (C-2'_{pyr}), 152.3 (C-6'_{pyr}) ppm. C₃₀H₂₄Cl₂N₄O₈S₂Zn: calcd. C 46.86, H. 3.15, N 7.29; found C 46.72, H 3.21, N 7.31.

[Hg{NNNtos(Qui)}₂](ClO₄)₂: The precipitation of the complex was obtained by lowering the temperature (0 °C). Yield 75% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{C-H} 3099.3, 3061.0, 2933.2, 2862.9, $\nu_{C=N}$ 1604.2, $\nu_{C=C}$ 1508.4, 1457.3, $\nu_{ClO_4^-}$ 1093.1 cm⁻¹. ¹H NMR (CD₃CN, *T* = 233 K): δ = methyl protons, 2.56 (s, 3 H, CH₃), aminomethyl protons 4.93, 5.79 (AB system, *J* = 14.3 and 4.8 Hz, *J*³_{H-Hg} = 8.1 Hz, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.26 (m, *J* = 6.7 Hz, 2 H, 5-H_{qui}), 7.55 (m, 7 H, 3'-H_{pyr}, 5'-H_{pyr}, 6-H_{qui}, H_{ar}), 8.00 (m, 2 H, 4'-H_{pyr}, 3-H_{qui}), 8.23 (d, *J* = 7.3 Hz, 1 H, 7-H_{qui}), 8.72 (d, *J* = 4.8 Hz, 1 H, 2'-H_{pyr}), 8.79 (d, *J* = 8.4 Hz, 1 H, 4-H_{qui}), 8.86 (dd, *J* = 4.0 and 1.5 Hz, *J*³_{H-Hg} = 9.7 Hz, 1 H, 2-H_{qui}) ppm. C₄₄H₃₈Cl₂HgN₆O₁₂S₂: calcd. C 44.85, H 3.25, N 7.13; found C 44.92, H 3.31, N 7.41.

[Cd{NNNtos(Qui)}₂](ClO₄)₂: The precipitation of the complex was obtained by lowering the temperature (0 °C). Yield 87% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{C-H} 3065.8, 2931.4, 2861.1, $\nu_{C=N}$ 1600.5, $\nu_{C=C}$ 1511.0, $\nu_{ClO_4^-}$ 1088.7 cm⁻¹. ¹H NMR (CD₃CN, *T* = 233 K): δ = methyl protons, 2.56 (s, 3 H, CH₃), aminomethyl protons 4.93, 5.93 (AB system, *J* = 14.1 Hz, *J*³_{H-Cd} = 4.3 Hz, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.30 (m, 2 H, 3'-H_{pyr}, 5-H_{qui}), 7.57 (m, 6 H, 5'-H_{pyr}, 6-H_{qui}, H_{ar}), 7.91 (td, *J* = 7.5 and 1.3 Hz, 1 H, 4'-H_{pyr}), 8.00 (dd, *J* = 4.4 and 8.3 Hz, 1 H,

3-H_{qui}), 8.25 (d, *J* = 7.9 Hz, 1 H, 7-H_{qui}), 8.52 (d, *J* = 6.0, *J*³_{H-Cd} = 9.8 Hz, 1 H, 2'-H_{pyr}), 8.84 (dd, *J* = 8.1 and 1.1 Hz, 1 H, 4-H_{qui}), 8.96 (dd, *J*³_{H-Cd} = 6.3 Hz, 1 H, 2-H_{qui}) ppm. C₄₄H₃₈CdCl₂N₆O₁₂S₂: calcd. C 48.47, H 3.51, N 7.71; found C 48.38, H 3.60, N 7.52.

[Zn{NNNtos(Qui)}₂](ClO₄)₂: The precipitation of the complex was obtained by addition of Et₂O. Diethyl ether was also used to wash the precipitate. Yield 92% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{C-H} 3058.6, 2936.2, 2857.3, $\nu_{C=N}$ 1606.7, $\nu_{C=C}$ 1505.3, 1464.8, $\nu_{ClO_4^-}$ 1091.4 cm⁻¹. ¹H NMR (CD₃CN, *T* = 227 K): δ = methyl protons, 2.56 (s, 3 H, CH₃), aminomethyl protons 5.00, 5.99 (AB system, *J* = 14.4 Hz, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.04 (d, *J* = 7.6 and 1.1 Hz, 2 H, 5-H_{qui}), 7.29 (t, 2 H, 3'-H_{pyr}), 7.55 (m, 6 H, 5'-H_{pyr}, 6-H_{qui}, H_{ar}), 7.94 (td, *J* = 7.7 and 1.5 Hz, 1 H, 4'-H_{pyr}), 8.10 (dd, *J* = 5.0 and 8.3 Hz, 1 H, 3-H_{qui}), 8.24 (d, *J* = 8.3 Hz, 1 H, 7-H_{qui}), 8.66 (d, *J* = 5.5 Hz, 1 H, 2'-H_{pyr}), 8.92 (dd, *J* = 8.4 and 1.3 Hz, 1 H, 4-H_{qui}), 8.96 (dd, *J* = 1.3 Hz, 1 H, 2-H_{qui}) ppm. C₄₄H₃₈Cl₂N₆O₁₂S₂Zn: calcd. C 50.66, H 3.67, N 8.06; found C 51.01, H 3.57, N 8.12.

Synthesis of Monochelate Dichloro Complexes

[Hg{NNN(Qui)}Cl₂]: A solution of HgCl₂ (0.065 g, 0.24 mmol) in methanol (2 mL) was added slowly to a stirred solution of NNN(Qui) (0.62 g, 0.26 mmol) in methanol (2 mL). The complex, which precipitated immediately, was filtered off, washed with toluene, pentane, and dried under vacuum. Yellow microcrystals were obtained (0.086 g, 0.17 mmol). Yield 70%. IR (KBr): $\tilde{\nu}$ = ν_{N-H} 3175.4, ν_{C-H} 3081.6, 3027.9, 2914.0 $\nu_{C=N}$ 1606.7, $\nu_{C=C}$ 1506.1 cm⁻¹. ¹H NMR (CD₃OD, *T* = 298 K): δ = aminomethyl protons, 4.71 (s, 2 H, pyr-N-CH₂), amine protons, 6.59 (br. s, 1 H, pyr-NH), pyridine and quinoline protons 7.07 (d, *J* = 7.3 Hz, 1 H, 7-H_{qui}), 7.44 (m, 3 H, 5-H_{qui}, 6-H_{qui}, 3'-H_{pyr}), 7.55 (d, *J* = 7.7 Hz, 1 H, 5'-H_{pyr}), 7.60 (dd, *J* = 8.3 Hz, 1 H, 3-H_{qui}), 7.89 (td, *J* = 7.7 and 1.8 Hz, 1 H, 4'-H_{pyr}), 8.31 (dd, *J* = 1.7 Hz, 1 H, 4-H_{qui}), 8.61 (d, *J* = 4.0 Hz, 1 H, 2'-H_{pyr}), 8.86 (dd, *J* = 4.2 Hz, 1 H, 2-H_{qui}) ppm. C₁₅H₁₃Cl₂HgN₃: calcd. C 35.55, H 2.59, N 8.29; found C 35.61, H 2.47, N 8.31.

The following complexes were synthesized in an analogous way using the appropriate ligand and chloride salts.

[Cd{NNN(Qui)}Cl₂]: Yield 82% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{N-H} 3144.4, ν_{C-H} 3045.7, 2927.2, $\nu_{C=N}$ 1604.4, $\nu_{C=C}$ 1505.7, 1479.3 cm⁻¹. ¹H NMR (CD₃CN, *T* = 333 K): δ = aminomethyl protons, 4.64 (s, 2 H, pyr-N-CH₂), amine protons, 5.15 (br. s, 1 H, pyr-NH), pyridine and quinoline protons 7.53 (m, 2 H, 5'-H_{pyr}, 3'-H_{pyr}), 7.75 (m, 2 H, 6-H_{qui}, 3-H_{qui}), 7.89 (m, 2 H, 5-H_{qui}, 7-H_{qui}), 7.98 (td, *J* = 7.7 and 1.7 Hz, 1 H, 4'-H_{pyr}), 8.55 (dd, *J* = 8.5 and 1.5 Hz, 1 H, 4-H_{qui}), 8.81 (d, *J* = 4.5 Hz, 1 H, 2'-H_{pyr}), 8.86 (dd, *J* = 4.4 Hz, 1 H, 2-H_{qui}) ppm. C₁₅H₁₃CdCl₂N₃: calcd. C 43.04, H 3.13, N 10.04; found C 43.09, H 3.20, N 10.11.

[Zn{NNN(Qui)}Cl₂]: Yield 84% (pale yellow microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{N-H} 3164.2, ν_{C-H} 3078.6, 3052.3, 2920.7, 2854.8, $\nu_{C=N}$ 1611.4, $\nu_{C=C}$ 1512.2, 1453.0 cm⁻¹. ¹H NMR (CD₃CN, *T* = 298 K): δ = aminomethyl protons, 4.70 (br. s, 2 H, pyr-N-CH₂), amine protons no signal, pyridine and quinoline protons 7.59 (m, 2 H, 5'-H_{pyr}, 3'-H_{pyr}), 7.78 (m, 2 H, 6-H_{qui}, 3-H_{qui}), 7.95 (m, 2 H, 5-H_{qui}, 7-H_{qui}), 7.98 (br. t, *J* = 7.4 Hz, 1 H, 4'-H_{pyr}), 8.63 (br. d, *J* = 8.3 Hz, 1 H, 4-H_{qui}), 8.95 (br. d, *J* = 4.7 Hz, 1 H, 2'-H_{pyr}), 9.24 (br. d, *J* = 3.8 Hz, 1 H, 2-H_{qui}) ppm. C₁₅H₁₃Cl₂N₃Zn: calcd. C 48.49, H 3.53, N 11.31; found C 48.62, H 3.49, N 11.20.

[Hg{NSN(Qui)}Cl₂]: Yield 89% (white microcrystals). IR (KBr): $\tilde{\nu}$ = ν_{C-H} 3027.9, 2954.2, 2880.4 $\nu_{C=N}$ 1600.0, $\nu_{C=C}$ 1499.4, 1486.0, 1439.1 cm⁻¹. ¹H NMR (CD₃CN, *T* = 298 K): δ = methylthio protons, 4.56 (s, 2 H, pyr-S-CH₂), pyridine and quinoline protons 7.38

(dd, $J = 4.4$ and 7.7 Hz, 1 H, 3'-H_{pyr}), 7.54 (d, $J = 7.7$ Hz, 1 H, 5'-H_{pyr}), 7.60 (t, $J = 8.1$ and 7.3 Hz, 1 H, 6-H_{qui}), 7.67 (dd, $J = 8.4$ and 4.4 Hz, 1 H, 3-H_{qui}), 7.82 (td, $J = 7.7$ and 1.8 Hz, 1 H, 4'-H_{pyr}), 7.90 (d, 1 H, 5-H_{qui}), 7.98 (d, 1 H, 7-H_{qui}), 8.42 (dd, $J = 1.8$ Hz, 1 H, 4-H_{qui}), 8.63 (d, 1 H, 2'-H_{pyr}), 9.06 (dd, 1 H, 2-H_{qui}) ppm. C₁₅H₁₂Cl₂HgN₂S: C 34.39, H 2.31, N 5.35; found C 34.12, H 2.27, N 5.51.

[Cd{NSN(Qui)}Cl₂]: Yield 91% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{C-H}$ 3072.0, 2966.7, 2907.5 $\nu_{C=N}$ 1597.8, $\nu_{C=C}$ 1499.1, 1485.9, 1459.6 cm⁻¹. ¹H NMR (CD₃CN, $T = 333$ K): δ = methylthio protons, 4.58 (s, 2 H, pyr-S-CH₂), pyridine and quinoline protons 7.35 (m, 2 H, 5'-H_{pyr}, 3'-H_{pyr}), 7.75 (m, 3 H, 6-H_{qui}, 3-H_{qui}, 4'-H_{pyr}), 8.03 (d, $J = 8.1$ Hz, 1 H, 5-H_{qui}), 8.30 (d, $J = 6.9$ Hz, 1 H, 7-H_{qui}), 8.42 (dd, $J = 8.5$ and 1.8 Hz, 1 H, 4-H_{qui}), 8.83 (d, $J = 4.9$ Hz, 1 H, 2'-H_{pyr}), 9.06 (dd, $J = 3.2$ Hz, 1 H, 2-H_{qui}) ppm. C₁₅H₁₂CdCl₂N₂S: calcd. C 41.35, H 2.78, N 6.43; found C 41.22, H 2.87, N 6.45.

[Zn{NSN(Qui)}Cl₂]: The precipitation of the complex was achieved by volume reduction followed by toluene addition. Yield 86% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{C-H}$ 3085.2, 3052.3, 2993.1, 2914.1, 2841.7 $\nu_{C=N}$ 1611.0, $\nu_{C=C}$ 1505.7, 1485.9, 1446.4 cm⁻¹. ¹H NMR (CD₃CN, $T = 298$ K): δ = methylthio protons, 4.58 (s, 2 H, pyr-S-CH₂), pyridine and quinoline protons 7.54 (m, 2 H, 5'-H_{pyr}, 6-H_{qui}), 7.80 (dd, $J = 5.5$ and 8.3 Hz, 1 H, 3'-H_{pyr}), 7.88 (dd, $J = 8.3$ and 4.9 Hz, 1 H, 3-H_{qui}), 7.99 (td, $J = 8.3$, 7.7 and 1.6 Hz, 1 H, 4'-H_{pyr}), 8.22 (dd, $J = 8.3$ and 1.4 Hz, 1 H, 5-H_{qui}), 8.40 (dd, $J = 7.4$ Hz, 1 H, 7-H_{qui}), 8.70 (dd, $J = 1.6$ Hz, 1 H, 4-H_{qui}), 9.11 (d, 1 H, 2'-H_{pyr}), 9.75 (dd, 1 H, 2-H_{qui}) ppm. C₁₅H₁₂Cl₂N₂SZn: C 46.36, H 3.11, N 7.21; found C 46.43, H 3.07, N 7.26.

[Hg{NNNtos(Qui)}Cl₂]: Yield 64% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{C-H}$ 3068.2, 2914.0 $\nu_{C=N}$ 1606.7, $\nu_{C=C}$ 1519.1 cm⁻¹. ¹H NMR (CD₃CN, $T = 233$ K): δ = methyl protons, 2.44 (s, 3 H, CH₃), aminomethyl protons 4.71 (s, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.29 (d, $J_{b-c} = 8.05$ Hz, 2 H, H_{ar}), 7.35 (t, $J = 5.1$ Hz, 1 H, 3'-H_{pyr}), 7.55 (m, 4 H, 5-H_{qui}, 6-H_{qui}, H_{ar}), 7.62 (m, 2 H, 5'-H_{pyr}, 3-H_{qui}), 7.84 (td, $J = 8.0$, 1.5 , and 8.4 Hz, 1 H, 4'-H_{pyr}), 7.99 (dd, $J = 7.9$ and 1.7 Hz, 1 H, 7-H_{qui}), 8.43 (dd, $J = 8.4$ and 1.8 Hz, 1 H, 4-H_{qui}), 8.51 (d, 1 H, 2'-H_{pyr}), 8.85 (dd, $J = 4.4$ Hz, 1 H, 2-H_{qui}) ppm. C₂₂H₁₉Cl₂HgN₃O₂S: calcd. C 39.98, H 2.90, N 6.36; found C 40.02, H 2.87, N 6.39.

[Cd{NNNtos(Qui)}Cl₂]: Yield 94% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{C-H}$ 3072.0, 2966.7, 2868.0 $\nu_{C=N}$ 1604.4, $\nu_{C=C}$ 1512.2, 1453.0 cm⁻¹. ¹H NMR (CD₃CN, $T = 333$ K): δ = methyl protons, 2.44 (s, 3 H, CH₃), aminomethyl protons 5.24 (s, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.33 (d, $J = 8.3$ Hz, 2 H, H_{ar}), 7.42 (m, 4 H, 3'-H_{pyr}, 6-H_{qui}, H_{ar}), 7.54 (d, $J = 5.1$ Hz, 1 H, 5-H_{qui}), 7.61 (d, 1 H, 5'-H_{pyr}), 7.72 (dd, $J = 4.1$ and 8.3 Hz, 1 H, 3-H_{qui}), 7.92 (td, $J = 6.2$ and 1.5 Hz, 1 H, 4'-H_{pyr}), 8.03 (dd, $J = 8.2$ and 1.0 Hz, 1 H, 7-H_{qui}), 8.52 (dd, $J = 1.5$ Hz, 1 H, 4-H_{qui}), 8.65 (d, $J = 6.2$ Hz, 1 H, 2'-H_{pyr}), 9.04 (dd, 1 H, 2-H_{qui}) ppm. C₂₂H₁₉CdCl₂N₃O₂S: calcd. C 46.13, H 3.34, N 7.34; found C 46.21, H 3.24, N 7.42.

[Zn{NNNtos(Qui)}Cl₂]: Yield 96% (white microcrystals). IR (KBr): $\tilde{\nu} = \nu_{C-H}$ 3065.4, 3032.5, 2960.1, 2927.2 $\nu_{C=N}$ 1617.6, $\nu_{C=C}$ 1512.2, 1492.5, 1439.9 cm⁻¹. ¹H NMR (CD₃OD, $T = 333$ K): δ = methyl protons, 2.40 (s, 3 H, CH₃), aminomethyl protons 5.32 (s, 2 H, pyr-N-CH₂), pyridine, quinoline, and aromatic protons 7.22 (d, $J = 7.9$ Hz, 2 H, H_{ar}), 7.27 (td, $J = 7.7$ and 1.1 Hz, 1 H, 3'-H_{pyr}), 7.48 (m, 4 H, 3-H_{qui}, 6-H_{qui}, H_{ar}), 7.59 (dd, $J = 7.4$ and 1.5 Hz, 1 H, 5-H_{qui}), 7.71 (d, $J = 7.7$ Hz, 1 H, 5'-H_{pyr}), 7.81 (td, $J = 1.7$ Hz, 1 H, 4'-H_{pyr}), 7.91 (dd, $J = 8.2$ Hz, 1 H, 7-H_{qui}), 8.31 (dd, $J = 8.4$ and 1.6 Hz, 1 H, 4-H_{qui}), 8.43 (d, $J = 4.7$ Hz, 1 H, 2'-H_{pyr}), 8.73 (dd,

1 H, 2-H_{qui}) ppm. C₂₂H₁₉Cl₂N₃O₂SZn: calcd. C 50.26, H 3.64, N 7.99; found C 50.32, H 3.73, N 8.05.

Potentiometric Titrations and Calculations: The potentiometric determinations were carried out by a Metrohm 654 pH-meter equipped with a Metrohm glass electrode calibrated at 25 °C by means of standard Metrohm buffer solutions (pH 4 and 7). All the measurements were carried out under N₂ stream in a thermostatted potentiometric cell.

The appropriate quantity of the ligands NSN(Py), NSN(Qui), and NNN(Qui) were poured into volumetric flasks (250 mL) and the appropriate volumes of HCl (0.1 M) were added to obtain NSN(Py)·2HCl, NSN(Qui)·2HCl, and NNN(Qui)·3HCl, respectively. Addition of NaCl (0.1 M) in water yielded the solutions at pre-determined concentration and ionic strength ([Ligand]· n HCl] = 1×10^{-3} M; $I = 0.1$ M).

An aliquot (50 mL) of the solution under study was then titrated with NaOH (0.1 M, $I = 0.1$ M). Evaluation of acid/base constants from the pH values vs. volume of NaOH added, was obtained by routines written using the SCIENTIST™ program. For calculation details see the Supporting Information.

Spectrophotometric Determination of the Complex Formation Constants: All the experiments were carried out in water (degassed under N₂ stream; pH \approx 6.5) and in thermostatted (25 °C) flasks. A standard stock of solutions (50 mL; 3×10^{-4} M) of the ligands [NNN(Qui), NSN(Qui), and NSN(Py)] was prepared by dissolving a weighted amount of the appropriate ligand in a volumetric flask and diluting to the mark with H₂O. The ligand solutions ($7-9 \times 10^{-5}$ M) used in the experiment were then prepared by dilution of the stock solution. The ligand solution was titrated by adding microaliquots of a standard solution of MCl₂ (M = Hg, Zn; [MCl₂] = 0.01 M) and Cd(ClO₄)₂ ([Cd(ClO₄)₂] = 0.5 M) by means of a micro-pipette. The ensuing absorbance values at different wavelengths were recorded at 25 °C and the evaluation of stepwise stability constants from the absorbance vs. volume of MCl₂ mL data was achieved by the speculative use of the program HYPERQUAD™.^[40] The expected total absorbance value (A_T) for each solution is given as $A_T = \sum_i \epsilon_i c_i$, where ϵ_i and c_i are the molar extinction coefficient and the concentration of the involved species, respectively. The iterative adjustment of calculated values of ϵ_{ML} and ϵ_{ML2} and subsequent refinement of the parameters was continued until the correlation matrix was minimized. The values of refined ϵ_L are in good agreement with the values measured by the Lambert-Beer experiment. UV/Vis titration spectra are reported in the Supporting Information.

The metal exchange spectrophotometric titrations were performed by addition of a weighted amount of Zn(ClO₄)₂·6H₂O ($1 \times 10^{-4} \leq [Zn(ClO_4)_2] \leq 1 \times 10^{-2}$ M) or of microaliquots of a standard stock solution (0.01 M) of Cd(ClO₄)₂·6H₂O to solutions of [Hg{NNN(Qui)}Cl₂] or [Zn{NNN(Qui)}]²⁺ (1×10^{-4} M), respectively. The absorbance values were taken at $\lambda = 250$ nm. The exchange constants from the absorbance vs. [M(ClO₄)₂] values were obtained by routines written using the SCIENTIST™ program. For calculation details see the Supporting Information.

X-ray Structural Determination: Well-formed crystals of the complexes [Hg{NSN(Qui)}Cl₂] (1), [Hg{NSN(Qui)}₂(OCIO₃)](ClO₄) (2), and [Zn{NNN(Qui)}Cl₂] (3) suitable for X-ray analysis, were mounted on the top of a glass fiber and transferred to either a STADI4 diffractometer equipped with a CCD camera (1, 2) or to a Nonius DIP-1030H system (3). The latter was generously made available by colleagues at the Department of Chemical Sciences of the University of Trieste, Italy. During the crystallization process,

Table 5. Selected bond lengths [Å] and bond angles [°] for the complexes 1–3.

	1		2		3	
	<i>TBPY-5-12-C</i>	<i>TBPY-5-12-A</i>				
Hg–Cl(1)	2.455(4)	2.494(4)	Hg–S	2.621(4)	Zn–Cl(1)	2.252(1)
Hg–Cl(2)	2.450(4)	2.428(4)	Hg–S'	2.749(5)	Zn–Cl(2)	2.343(1)
Hg–S	2.759(4)	2.748(3)	Hg–N(1)	2.63(1)	Zn–N(1)	2.124(3)
Hg–N(1)	2.350(9)	2.38(1)	Hg–N(1')	2.23(1)	Zn–N(2)	2.234(3)
Hg–N(2)	2.44(1)	2.44(1)	Hg–N(2)	2.28(1)	Zn–N(3)	2.156(3)
			Hg–O(1')	2.60(1)		
Cl(1)–Hg–Cl(2)	105.7(1)	106.0(1)	S–Hg–S'	111.4(1)	Cl(1)–Zn–Cl(2)	111.9(1)
Cl(1)–Hg–S	163.1(1)	156.5(1)	S–Hg–N(1)	74.0(3)	Cl(1)–Zn–N(1)	105.3(1)
Cl(1)–Hg–N(1)	97.5(3)	93.8(3)	S–Hg–N(1')	118.2(4)	Cl(1)–Zn–N(2)	104.8(1)
Cl(1)–Hg–N(2)	94.6(3)	89.4(3)	S–Hg–N(2)	78.0(3)	Cl(1)–Zn–N(3)	105.9(1)
Cl(2)–Hg–S	90.8(1)	97.1(1)	S–Hg–O(1')	144.1(3)	Cl(2)–Zn–N(1)	94.6(1)
Cl(2)–Hg–N(1)	128.0(3)	128.1(3)	S'–Hg–N(1)	170.6(3)	Cl(2)–Zn–N(2)	143.2(1)
Cl(2)–Hg–N(2)	127.6(2)	129.7(3)	S'–Hg–N(1')	76.3(3)	Cl(2)–Zn–N(3)	92.6(1)
S–Hg–N(1)	74.7(3)	74.7(3)	S'–Hg–N(2)	105.2(3)	N(1)–Zn–N(2)	77.0(1)
S–Hg–N(2)	71.6(3)	72.2(3)	S'–Hg–O(1')	101.4(3)	N(1)–Zn–N(3)	142.6(1)
N(1)–Hg–N(2)	95.2(3)	97.2(4)	N(1)–Hg–N(1')	94.5(4)	N(2)–Zn–N(3)	75.3(1)
			N(1)–Hg–N(2)	83.2(4)		
			N(1)–Hg–O(1')	75.7(4)		
			N(1')–Hg–N(2)	162.4(4)		
			N(1')–Hg–O(1')	82.7(4)		
			N(2)–Hg–O(1')	79.9(4)		

complex **2** forms crystals that are either colorless or ruby-red. The data presented here refer to the ruby-red specimen, as the colorless crystals proved inadequate for the X-ray experiment.

The X-ray diffraction data were collected at room temperature using graphite-monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects (**1–3**) and for absorption (**1, 2**). For **3**, a total of 36 frames were collected, each with a rotation of 6° about ϕ , an exposure time of 20 min, and the detector position at 90 mm from the crystal, whereas data reduction and cell refinement were carried out using the programs DENZO and SCALEPACK.^[45] The structures were solved by means of the heavy-atom methods (**1, 2**) or the direct methods (**3**), using the SHELXTL-NT package,^[46] and were refined by full-matrix least-squares procedure on F^2 with the SHELXL-97^[47] program. Scattering factors incorporated in SHELXL-97 were used; no empirical extinction corrections were applied.

In the last cycles of refinement of **1** and **3**, all the non-H atoms were allowed to vibrate anisotropically. In **2** the ratio between the number of observed reflections and the number of parameters was unsatisfactory. Accordingly, the atoms belonging to the inner coordination core were refined anisotropically, while the remaining non-H atoms were refined isotropically. As for H atoms, in **1** and **2** they were placed in idealized positions and refined with the “riding model.” In both structures the U_{iso} values of hydrogen atoms were set at 1.2 times U_{eq} of the appropriate carrier atom. In **3**, the H atoms were refined isotropically. The crystal data and refinement parameters of the three complexes are summarized in the Supporting Information (Table S1); none of the structures revealed any anomalous feature. Selected interatomic distances and angles are shown in Table 5.

CCDC-642237 to -642239 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Details on acidity macro- and micro-constant and stability constant determination, UV/Vis spectra of the spectrophotometric titrations, X-ray crystallographic data.

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