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Anion-Directed Template Synthesis and Hydrolysis of Mono-Condensed Schiff Base of 1,3-Pentanediamine and *o*-Hydroxyacetophenone in Ni^{II} and Cu^{II} Complexes

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Bis(*o*-hydroxyacetophenone)nickel(II) dihydrate, on reaction with 1,3-pentanediamine, yields a bis-chelate complex $[NiL_2]\cdot 2H_2O$ (**1**) of mono-condensed tridentate Schiff base ligand HL {2-[1-(3-aminopentylimino)ethyl]phenol}. The Schiff base has been freed from the complex by precipitating the Ni^{II} as a dimethylglyoximato complex. HL reacts smoothly with $Ni(SCN)_2\cdot 4H_2O$ furnishing the complex [NiL(NCS)] (**2**) and with $CuCl_2\cdot 2H_2O$ in the presence of NaN_3 or NH_4SCN producing $[CuL(N_3)]_2$ (**3**) or [CuL(NCS)] (**4**). On the other hand, upon reaction with $Cu(ClO_4)_2\cdot 6H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$, the Schiff base undergoes hydrolysis to yield ternary complexes $[Cu(hap)(pn)(H_2O)]ClO_4$ (**5**) and $[Cu(hap)(pn)(H_2O)]NO_3$ (**6**), respectively (Hhap = *o*-hydroxyacetophenone and pn = 1,3-pentanediamine). The ligand HL undergoes hydrolysis also on reaction with $Ni(ClO_4)_2\cdot 6H_2O$ or $Ni(NO_3)_2\cdot 6H_2O$ to yield $[Ni(hap)_2]$ (**7**). The structures of the complexes **2**, **3**, **5**, **6**, and **7** have been confirmed by single-crystal X-ray analysis. In complex **2**, Ni^{II} possesses square-planar geometry, being coordinated by the tridentate mono-negative Schiff base, L and the isothiocyanate group. The coordination environment around Cu^{II} in complex **3** is very similar to that in complex **2** but here two units are joined together by end-on, axial-equatorial azide bridges to result in a dimer in which the geometry around Cu^{II} is square pyramidal. In both **5** and **6**, the Cu^{II} atoms display the square-pyramidal environment; the equatorial sites being coordinated by the two amine groups of 1,3-pentanediamine and two oxygen atoms of *o*-hydroxyacetophenone. The axial site is coordinated by a water molecule. Complex **7** is a square-planar complex with the Ni atom bonded to four oxygen atoms from two hap moieties. The mononuclear units of **2** and dinuclear units of **3** are linked by strong hydrogen bonds to form a one-dimensional network. The mononuclear units of **5** and **6** are joined together to form a dimer by very strong hydrogen bonds through the coordinated water molecule. These dimers are further involved in hydrogen bonding with the respective counteranions to form 2-D net-like open frameworks.

Introduction

The development of routes to unsymmetrical N,O donor ligands is of interest since such ligands may be useful in preparing synthetic analogues of the metal-binding sites of zinc and copper proteins.[1] Recently, this class of compounds has also attracted much attention in the field of optoelectronic technologies for their large nonlinear responses.[2] Synthesis of the mono-condensation products of diamines and acetylacetone or salicylaldehyde derivatives, hereafter referred to as “half units”, where one primary amine group forms an imine or enamine bond and the other is unchanged, is the most challenging step for the construction of such unsymmetrical ligands. These half units are also very useful for the design and synthesis of several di- and trinuclear metal complexes.[3] These complexes are valuable to theoretical and experimental chemists, as the steric and electronic factors of the Schiff base can be tuned systematically by introducing suitable substituents to bring about subtle structural variations that are extremely useful to deduce a relation between magnetic coupling and structural features.[3] These half units have been synthesized by several routes.[4–7] The most convenient one is the condensation under high dilution in chloroform as described by Costes et al.[8] However, this procedure is effective only for condensation of acetylacetone or its derivatives with various diamines.[3b,3e,7,9] In the case of aromatic aldehydes or ketones (salicylaldehyde or its derivatives), the synthesis of the half unit by using a large excess of diamines is straightforward but problems of purification appeared formidable. Elder reported a very convenient template synthesis of the nickel(II) complex for the half unit of salicylaldehyde with 1,3-propanediamine, 1,4-butanediamine, or 2,5-dimethyl-2,5-hexanediamine.[10] The ligand was freed by precipitating the Ni^{II} as a DMG complex (H_2DMG = dimethylglyoxime) and was used to synthesize asymmetric tetradentate ligands or complexes with another metal ion.[3a,3h,11] Similar ligands and their copper complexes have been obtained with

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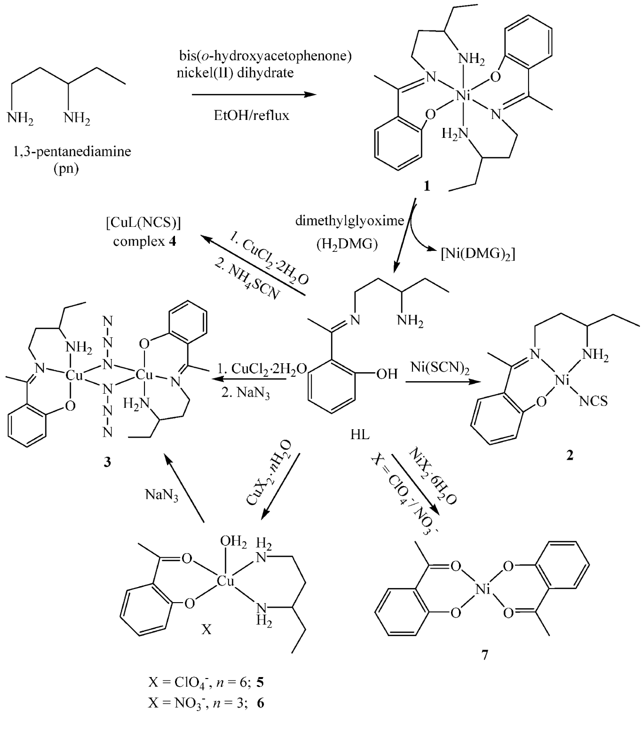
the help of the copper template effect.[3g] The synthesis is even easier with the use of ketone (hydroxyacetophenone) instead of aldehyde and with a substituted diamine.[9] However, for nickel complexes, the problem is more complicated and Elder's method is more appropriate.

We investigate here if Elder's procedure can be taken as a general method for the synthesis of half units. For this purpose, we use three diamines, 1,2-ethanediamine, 1,2-propanediamine, and 1,3-pentanediamine and try to obtain the half unit with *o*-hydroxyacetophenone by following Elder's procedure. We succeeded in synthesizing the desired Ni^{II} bis-chelate only in the case of 1,3-pentanediamine. The ligand was freed as usual by using H_2DMG and used to synthesize complexes with nickel(II) thiocyanate/perchlorate/nitrate and copper(II) azide/thiocyanate/perchlorate/nitrate. All but one of the resulting complexes were characterized by single-crystal X-ray analysis. In the case of nickel(II) thiocyanate and copper(II) azide/thiocyanate, we obtained the complexes of the desired ligand but for the other salts, the ligand undergoes hydrolysis to yield ternary complexes for Cu^{II} and the binary complex, $Ni(hap)_2$ for Ni^{II} (Hhap = *o*-hydroxyacetophenone) (Scheme 1). The formation of a Schiff base by condensation of diamine and carbonyl compounds is well known.[3–10] The reverse process, i.e., hydrolysis of a Schiff base in the presence of a metal ion has been observed recently by us,[12] but the probable reasons are still unknown. In this study, we observe for the first time that the formation or hydrolysis of the mono-condensed N,O donor Schiff base is directed by the counteranion. The observations led us to put forward a hypothesis for the explanation of the process considering the fulfillment of the coordination numbers and geometry of the corresponding metal ions. The hypothesis is also extended to rationalize the failure in obtaining the analogous nickel(II) bis-chelate complex of the mono-condensed Schiff base of 1,2-ethanediamine and 1,2-propanediamine and also to the copper template synthesis of Schiff bases.[3g,9]



Scheme 1.

Results and Discussion

Template Synthesis of the Ligand, Formation of Its Complexes, and Its Hydrolysis

The mono-condensed ligand, 2-[1-(3-aminopentylimino)-ethyl]phenol (HL) has been prepared conveniently as the nickel complex, $[NiL_2]\cdot 2H_2O$ (**1**), by the reaction of bis(*o*-hydroxyacetophenone)nickel(II) dihydrate and 1,3-pentanediamine (pn) (see Exp. Sect.). However, adopting a similar procedure, we have failed to synthesize analogous nickel(II) complexes by using 1,2-ethanediamine or 1,2-propanediamine. In both cases, the resulting species were the square-planar Ni^{II} complexes of the corresponding di-Schiff base [2:1 condensate of *o*-hydroxyacetophenone (Hhap) and the diamine]. The free ligand (HL) was isolated by removing nickel as bis(dimethylglyoximato)nickel(II) from complex **1**. HL reacts smoothly with $Ni(SCN)_2\cdot 4H_2O$, furnishing the monomeric square-planar Ni^{II} complex [NiL(NCS)] (**2**) and also reacts with $CuCl_2\cdot 2H_2O$ in the presence of NaN_3 to yield the end-on azido-bridged dimeric complex $[CuL(N_3)]_2$ (**3**). We have also added HL to a methanol solution of Cu^{II} chloride followed by NH_4SCN and have obtained Cu^{II} complex [CuLNCS] (**4**) as is evident from spectral and elemental analysis. The ligand remains intact in complexes **2**, **3**, and **4**. On the other hand, when HL is allowed to react with $Cu(ClO_4)_2\cdot 6H_2O$ or $Cu(NO_3)_2\cdot 3H_2O$, it undergoes hydrolytic cleavage to form ternary copper(II) complexes, $[Cu(hap)(pn)(H_2O)]ClO_4$ (**5**) and $[Cu(hap)(pn)(H_2O)]NO_3$ (**6**), which consist of both the parent 1,3-pentanediamine and *o*-hydroxyacetophenone. Complex **3** does not react with NEt_4ClO_4 or NMe_4NO_3 but complex **5** or **6** reacts readily with NaN_3 in methanol solution to yield **3** (Scheme 1). On the contrary, reaction of HL with $Ni(ClO_4)_2\cdot 6H_2O$ or $Ni(NO_3)_2\cdot 6H_2O$ under similar conditions resulted in immediate separation of a red solid, which was characterized by single-crystal X-ray analysis and was identified as $[Ni(hap)_2]$ (**7**). On slow evaporation of the filtrate, the corresponding bis-diamine complexes of Ni^{II} were obtained. Therefore, it is clear that in the presence of the perchlorate or nitrate salt of Ni^{II} the Schiff base undergoes hydrolysis like the analogous Cu^{II} salt.

The formation of the Schiff base complexes with nickel(II) thiocyanate and copper(II) azide or thiocyanate and their hydrolytic cleavage during complex formation with nitrate or perchlorate salts of Cu^{II}/Ni^{II} can be rationalized in the light of the templating effect of the metal ion modulated by the counteranions. A templating agent can be said to contain the required information to organize a collection of building blocks so that they can be linked together in a specific manner.[13] It is well known that Ni^{II} prefers six-coordinate octahedral geometry with weak-field ligand sets and four-coordinate square-planar geometry with strong-field ligand sets. In complex **2**, the strongly coordinating thiocyanate and three donor atoms from the Schiff base complete the square-planar geometry around Ni^{II}. Cu^{II}, being a d^9 system, is liable to undergo Jahn–Teller distortion, which results in an elongated octahedral (4+2) coordination. The strong-field ligands coordinate to the four equatorial sites, leaving the two axial sites vacant or to be occupied by weakly coordinating ligands (e.g., solvent molecules). In **3** (or its thiocyanate analogue, **4**), the two strong-field ligands, azide (or thiocyanate) and the tridentate Schiff base conveniently coordinate to the four equatorial sites. However, nitrate or perchlorate ions which are rather weakly coordinating ligands, abstain from being coordinated in the equatorial position of Cu^{II}. Instead, the Schiff base undergoes hydrolysis to yield two bidentate strong-field chelating ligands which can occupy four equatorial sites. In short, in each of **2**–**7**, there are four coordination sites to be occupied preferably by the four strong-field donor sets. In **2**, **3**, and **4** the respective strong-field anion and the Schiff base ligand can satisfy that requirement, but in **5**, **6**, and **7**, as the anions are weakly coordinating, the Schiff base undergoes hydrolysis to generate one more strong-field donor site. In this context, it is to be noted that the acidity of the metal ion is well known to catalyze such hydrolysis,[14] and one may think of a simpler explanation: if a quick precipitation occurs, as in the azide or thiocyanate cases, the expected complex is recovered, while if there is no immediate precipitation, the metal acidity has enough time to induce hydrolysis and then the complex resulting from the diamine and hydroxyacetophenone is isolated in crystalline form. To verify this, we synthesized complexes **5** and **6** in a medium made basic by addition of triethylamine, but observed the same hydrolysis phenomenon. Moreover, conversion of **5** and **6** to **3** by the addition of NaN_3 in methanol solution, as well as the immediate separation of $[Ni(hap)_2]$ (**7**) on addition of HL to $Ni(ClO_4)_2{\cdot}6H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$ confirm that the time needed for separation of the complex in the solid state is not the decisive factor for ligand hydrolysis in the present case. However, the possibility of the presence of an equilibrium, which may shift during the crystallization toward the less soluble species, can not be ruled out and seems to be imperative for isolation of ternary complexes **5** and **6** instead of simple $Cu(hap)_2$ like its Ni^{II} analogue (**7**). The Cu^{II}-templated mono-condensation of diethylenetriamine with salicylaldehyde from an intermediate pentacoordinate, ternary Cu^{II} complex but double-condensation of ethylenediamine from a relatively stable square-planar intermediate species under the same reaction conditions was observed by Rotondo et al.[15] and is in good agreement with the proposed hypothesis.

The same hypothesis may be extended to explain the failure of the formation of the mono-Schiff base complexes of 1,2-ethanediamine and 1,2-propanediamine templated by Ni^{II}. Both the X-ray structural data and theoretical calculations indicate that in the Schiff base of 1,2-ethanediamine and its derivatives, which form a five-membered chelate ring with the metal ion, the M–N bond lengths are shorter than those formed by the 1,3-propanediamine or 1,4-butanediamine derivatives which form six- or seven-membered chelate rings, respectively.[16] As a result, with Ni^{II}, the Schiff base derived from 1,2-ethanediamine and its derivatives form square-planar complexes, whereas those derived from higher-membered-ring diamines form octahedral complexes as the former exert higher crystal field stabilization energy. Therefore, it is logical to assume that the stability of the square-planar geometry is the driving force for the formation of di-Schiff complexes of Ni^{II} with 1,2-ethanediamine and its derivatives, and the octahedral geometry, which is conveniently satisfied by two tridentate Schiff bases, stabilizes the mono-Schiff base ligands of the diamine that forms higher-membered rings. In this context, one may note that the success of Elder in synthesizing the mono-condensed Schiff base seems to lie in his choice of diamines (1,3-propanediamine, 1,4-butanediamine, or 2,5-dimethyl-2,5-hexanediamine), all of which form either a six- or seven-membered chelate ring with Ni^{II}. A similar explanation is also found to be valid for the formation of mono- and di-Schiff base complexes of Ni^{II} with diamines and pyridine-2-carbaldehyde[17] and also for the copper(II) template synthesis of the half unit in the presence of other coordinating groups (pyridine, imidazole etc) by Costes et al.[3g]

IR and UV/Vis Spectra of the Complexes

In the IR spectra of complex **1** the two primary NH_2 stretching modes are seen at 3344 and 3205 cm^{-1} as sharp bands (doublet) for the asymmetric and symmetric vibrations, respectively. Generally, stretching vibration for water appears above 3400 cm^{-1}. Hence the appearance of a band near 3434 cm^{-1} indicates the presence of a water molecule. A strong and sharp band due to azomethine ν(C=N) appears at 1612 cm^{-1}. In complex **2**, the asymmetric and symmetric stretching vibrations for the free NH_2 appear at 3205 and 3084 cm^{-1}. A strong absorption band at 2093 cm^{-1} corroborates the presence of an N-bonded thiocyanate group in the complex.[21] The band due to azomethine ν(C=N) appears at 1596 cm^{-1}. Complex **3**, shows only a single absorption band, consistent with the presence of only one type of azide bridge in the structures and it appears at lower frequency, 2043 cm^{-1} in agreement with the asymmetric bridging.[3d,3h] The band due to azomethine ν(C=N) appears at 1589 cm^{-1} and that of free NH_2 appears at 3261, 3203, and 3128 cm^{-1}. In complex **4**, the asymmetric and symmetric stretching vibrations for the free NH_2 appear at 3208 and 3148 cm^{-1}, the band due to azomethine ν(C=N) appears at 1591 cm^{-1}, and a strong absorption band at 2104 cm^{-1} corroborates the presence of a N-bonded thiocyanate group in the complex.[16d,21]

Complex **5** shows a strong and broad band centered at 3508 cm^{-1} due to the presence of a water molecule. The stretching vibrations due to free NH_2 groups of the amine ligand appear at 3328 cm^{-1} and 3263 cm^{-1}. In complex **6**, a strong and broad band centered at 3490 cm^{-1} appears due to the presence of a water molecule, and the stretching vibrations due to free NH_2 groups of the amine ligand appear at 3318 and 3257 cm^{-1}. The region around 1600 cm^{-1} of these complexes is different from that of **1**–**4** due to the presence of a very intense band for carbonyl stretching at 1612 cm^{-1}. In complexes **5** and **6**, the characteristic, strong peaks for stretching vibrations of uncoordinated perchlorate at 1088 cm^{-1} (ν_3) and 948 cm^{-1} (ν_4) and nitrate at 1434 cm^{-1} (ν_5), 1375 cm^{-1} (ν_1), and 1032 cm^{-1} (ν_2) are noted. Complex **7**, shows a very intense band for C=O (ketone) stretching at 1571 cm^{-1} and a medium strong band at 1240 cm^{-1}, which is assigned to the C–O (phenoxy) stretching frequency.[18]

The electronic absorption spectra in acetonitrile solution and solid-state reflectance spectra of all the complexes are recorded. No significant differences are observed, indicating that the molecular structure of the complexes in solution remains the same as in the solid state. For complex **1** a broad band near 980 nm, well separated from the second transition at about 561 nm is observed as is usual for octahedral Ni^{II}. The higher energy d–d band is obscured by a strong charge-transfer transition. Complexes **2** and **7** show only one band at 474 nm and 458 nm respectively, indicating a large crystal-field splitting and consistent with the square-planar geometry of the Ni^{II} complexes. The electronic absorption spectra of complexes **3**, **4**, **5**, and **6** show a single absorption band at 602, 586, 594, and 595 nm, respectively. The bands are typical of d–d transitions in the square-pyramidal environment around Cu^{II}.[3] In complex **3**, the azide-to-Cu^{II} charge-transfer band (LMCT) is observed at 379 nm.

Thermal Analysis of Complexes 1, 5, and 6

The simultaneous TG-DTA curves for complex **1** reveal that upon heating it starts to lose water molecules at 80 °C and becomes dehydrated at ca. 110 °C in a single step. The observed weight loss (7.6%) corroborates the loss of two water molecules (calcd. 7.28%). The compound does not show any color change on deaquation. Complex **5** starts to lose water molecules at ca. 55 °C and becomes dehydrated at ca. 130 °C in a single step. Complex **6** starts to lose water molecules at ca. 65 °C and becomes dehydrated at ca. 120 °C in a single step. In both the complexes, the observed weight loss (5.0% in **5** and 5.7% in **6**) corroborates the loss of one water molecule (calcd. 4.3% in **4** and 4.7% in **5**) as observed in the X-ray structural analysis.

Electrochemical Study

The cyclic voltammograms of complexes **1**, **3**, **4**, **5**, **6**, and **7** are recorded in the potential range +1.2 to –1.2 V. The cyclic voltammograms of complex **1** are recorded in methanol solution (Pt electrode) under nitrogen, and the diagram is shown in Figure 1. As is evident from this figure, it shows only a single oxidation peak (Ni^{2+}/Ni^{3+}) at 0.52 V during the anodic potential scan. During the return cathodic potential scan, just after the oxidation peak, a cathodic peak is observed at 0.38 V. The ratio of ip_c/ip_a remains close to 1 at scan rates of 0.05 to 0.2 V s^{-1}. The separation between the cathodic and anodic peak potentials (ΔE_P = 140 mV) indicates a quasi-reversible redox process assignable to the Ni^{II}/Ni^{III} couple with $E_{1/2}$ = 0.45 V (vs. SCE). Similar oxidative responses have also been found in several other octahedral Schiff base complexes of Ni^{II}.[3a,19] Complex **2** is only slightly soluble in the solvents which are commonly used for electrochemical study and therefore, electrochemical study can not be performed for this compound. Complex **7** does not give any reductive or oxidative response in the above-mentioned potential range.

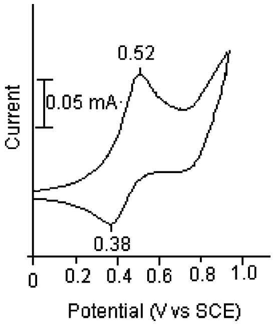


Figure 1. The cyclic voltammogram of **1** in methanol solution (scan rate 100 mV s^{-1}).

The cyclic voltammograms of complexes **3** and **4** are recorded in acetonitrile solution (Pt electrode) under nitrogen. They do not give any oxidative response but show electrochemically quasi-reversible reductive responses. The voltammograms show a cathodic peak (E_{pc}) at –0.52 and –0.59 V with an anodic counterpart (E_{pa}) at –0.34 and –0.40 V [$E_{1/2}$ = –0.43 V and 0.49 V (vs. SCE)] for **3** and **4**, respectively, possibly due to the Cu^{II}/Cu^{I} couple. In both the complexes, the quasi-reversibility has been assessed from the large peak-to-peak separation (ΔE_P = 180 mV and 190 for complexes **3** and **4**, respectively).

Complexes **5** and **6** in acetonitrile solution display a reductive response attributed to the Cu^{II}/Cu^{I} couple at –0.42 V (Ep_c) and –0.38 V (Ep_c) vs. SCE for **5** and **6**, respectively, during the cathodic potential scan. On reversing the potential scan just after completion of the peak, an anodic response at –0.32 V with a very narrow width and high peak current was observed. The response is typical of anodic stripping of copper.[20] Therefore, it may be assumed that on the electrode surface the Cu^{II} complexes, **5** and **6** are reduced to Cu^{I} which are not stable and undergo disproportionation to Cu^0 and Cu^{2+}.

Description of Structures of the Complexes

Complex 2

The structure of **2** is shown in Figure 2, and the selected bond lengths and angles are summarized in Table 1. The discrete molecule contains the metal in a four-coordinate, square-planar environment with three ligating atoms O(1), N(1), and N(2) of the mono-negative Schiff base along with the nitrogen atom N(3) of a thiocyanate group. The deviations of the four donor atoms O(1), N(1), N(2), and N(3) from their least-squares mean plane through them are –0.046(4), 0.039(4), –0.044(4), and 0.040(4) Å, respectively. The Ni atom deviates from the mean plane by 0.0107(7) Å. The tetrahedral distortion is apparent since one pair of diagonal donor atoms clearly lies below the plane while the other pair is above the plane with the metal ion nearly in the mean plane. The dihedral angles between the two planes [N(l)–Ni(1)–O(1) and N(2)–Ni(1)–N(3)] is 3.6(1)° compared with 0° for a perfectly square-planar arrangement and 90° for a perfect tetrahedral arrangement. The two diagonal N(2)–Ni(1)–O(1) and N(1)–Ni(1)–N(3) angles of the complex [176.7(2) and 178.0(2)°] are less than 180° as a result of this tetrahedral distortion. The Ni–N(imine) bond length is shortest [1.872(4) Å] and the Ni–N(amine) distance is the longest [1.905(6) Å]; the average Ni–N bond length is longer than the Ni–O distance as is usual for complexes of this type of ligand.[3a] The Ni(1)–N(3)–C(14) angle of 160.8(5)° is usual for terminally coordinated N-bonded thiocyanate.[16d,21] The six-membered ring comprising Ni(1)–N(1)–C(7)–C(6)–C(1)–O(1), adopts a screw-boat conformation while the other six-membered chelate ring Ni(1)–N(1)–C(9)–C(10)–C(11)–N(2), containing the diamine fragment assumes a boat conformation. One of the hydrogen atoms H(2b) of the amine nitrogen N(2) is involved in strong hydrogen bonding with the hydroxy oxygen atom O(1)′ of a neighboring unit (′ = –1 + *x*, *y*, *z*) to form an infinite 1-D hydrogen-bonded chain as shown in Figure S1.

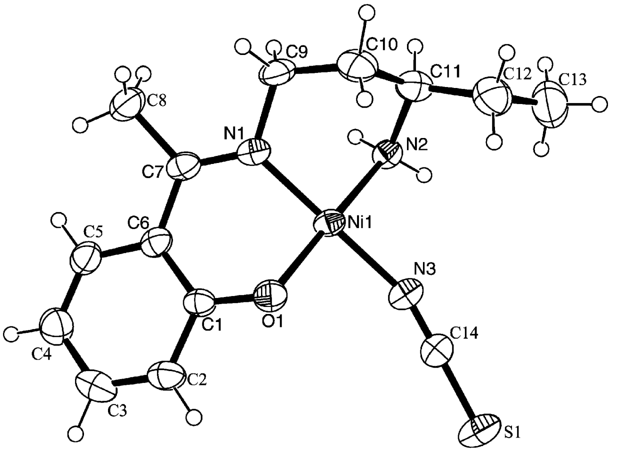


Figure 2. ORTEP-3 view of complex **2** with atom-numbering scheme (50% thermal ellipsoids).

Table 1. Selected bond lengths [Å] and bond angles [°] for complex **2**.

Ni1–O1	1.834(4)	O1–Ni1–N1	91.2(1)
Ni1–N1	1.872(4)	N1–Ni1–N2	90.0(1)
Ni1–N2	1.905(6)	N2–Ni1–N3	90.9(2)
Ni1–N3	1.885(5)	O1–Ni1–N3	88.0(1)
		O1–Ni1–N2	176.7(2)
		N1–Ni1–N3	178.0(2)

In this context, it is worthwhile to compare the structure of **2** with that of a reported dinuclear compound[3a] having a very similar Schiff base ligand, prepared by 1:1 condensation of salicylaldehyde and 1,3-propanediamine. In the reported complex, two equivalent nickel atoms have distorted octahedral environments and the dinuclear entity is formed through one aqua-bridge and two μ_2-phenoxido groups of the Schiff base. Hence, it is interesting to note that small differences in the steric and electronic factors of the Schiff base unit can cause a remarkable change in the molecular structure of the complexes.

Complex 3

The structure determination reveals that complex **3** consists of a centrosymmetric dinuclear species $[Cu_2L_2(N_3)_2]$ as shown in Figure 3. Selected bond lengths and angles are summarized in Table 2. Within the dimeric units each of the copper(II) centers is coordinated by three ligating atoms, O(11), N(19), and N(23), of the mono-negative Schiff base ligand along with a nitrogen atom, N(1), of one of the bridging azides; this comprises the basal plane. A second nitrogen atom, N(1)′ (′ = 1 –*x*, 2 – *y*, 2 – *z*) from the centro-

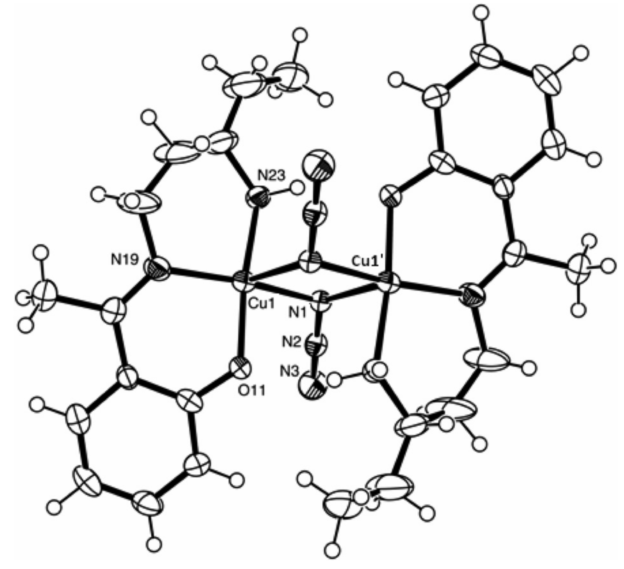


Figure 3. ORTEP-3 view of complex **3** with atom-numbering scheme (30% thermal ellipsoids); atoms marked with (′) are transformed by the symmetry element 1 – *x*, 2 – *y*, 2 – *z*.

Table 2. Selected bond lengths [Å] and bond angles [°] for complex **3**.

Cu(1)–O(11)	1.889(2)	O(11)–Cu(1)–N(19)	91.4(1)
Cu(1)–N(19)	1.977(3)	O(11)–Cu(1)–N(23)	170.1(1)
Cu(1)–N(23)	1.984(3)	N(19)–Cu(1)–N(23)	97.5(1)
Cu(1)–N(1)	2.059(3)	O(11)–Cu(1)–N(1)	86.7(1)
Cu(1)–N(1)′	2.451(3)	N(19)–Cu(1)–N(1)	166.6(1)
		N(23)–Cu(1)–N(1)	83.6(1)
		O(11)–Cu(1)–N(1)′	90.7(1)
		N(19)–Cu(1)–N(1)′	103.0(1)
		N(23)–Cu(1)–N(1)′	91.6(1)
		N(1)–Cu(1)–N(1)′	90.3(1)

Symmetry element: ′ = 1 – *x*, 2 – *y*, 2 – *z*.

symmetrically related bridging azide coordinates axially at a rather long distance [2.451(3) Å], furnishing an elongated square-pyramidal (4 + 1) geometry for each copper(II) center. The bridging Cu–N–Cu′ angle is 89.7(1)°. The bridging Cu_2N_2 network is exactly planar as is dictated by symmetry. The bridging N_3^- anions are quasi-linear with the N–N–N angles at 178.8(8)°. All the bond lengths and angles are within the range of those found in similar end-on azido-bridged copper(II) complexes of the tridentate Schiff bases.[3d,3e,11] The four basal donor atoms [O(11), N(19), N(23), and N(1)] deviate from the mean coordination plane through them by –0.063(2), 0.116(4), –0.057(3), and 0.120(3) Å, respectively. As is usual for a square-pyramidal structure, the copper atom is slightly pulled out of the mean square plane towards the apical donor atom at a distance 0.116(2) Å. The distortions of the coordination polyhedron from the square pyramid to the trigonal bipyramid have been calculated by the Addison parameter (τ)[22] as an index of the degree of trigonality. τ is defined as $(\beta - \alpha)/60$ where β and α are the two *trans*-basal angles. For a perfectly square pyramid geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry. The addition parameter ($\tau = 0.06$) for the complex indicates that the distortion towards trigonal bipyramid geometry is very small. The six-membered chelate rings comprising Cu(1)–N(19)–C(20)–C(21)–C(22)–N(23) and Cu–O(11)–C(12)–C(17)–C(18)–N(19) adopt a boat and a screw-boat conformation, respectively.

There are two amine hydrogen atoms [H(23a) and H(23b)], and both are involved in hydrogen bond formation. H(23a) forms a strong intra-dimer hydrogen bond with the phenoxy oxygen O(11)′ (′ = 1 – *x*, 2 – *y*, 2 – *z*). Formation of such an intra-dimer hydrogen bond that holds the two units together along with the end-on azido bridge is a common feature of this type of complex.[3d,3e,11] In addition, the dinuclear entities are linked by another hydrogen bond through H(23b) of the one dinuclear entity and the nitrogen atom N(3)′ of the azide of the neighboring dinuclear entity resulting in a one-dimensional supramolecular structure as shown in Figure S2.

Complexes 5 and 6

Both complexes **5** and **6** show a similar coordinating arrangement of the donor atoms around the central copper ion. The structures as shown in Figures 4 and S3 contain the metal in a five-coordinate, square-pyramidal environment in which N(1) and N(2) of the 1,3-pentanediamine moiety and O(1) and O(2) of deprotonated *o*-hydroxyacetophenone constitute the basal plane. The axial position is occupied by O(3) of a water molecule at a distance of 2.369(2) and 2.336(2) Å for **5** and **6**, respectively. All the bond lengths and bond angles of both complexes are within the expected ranges and are summarized in Table 3. In both complexes the Cu(1)–O(1) (phenoxy) distance is significantly shorter than the Cu–O2 (ketone) distances, corroborating the stronger coordinating ability of the phenoxy group. The deviations of the four basal donor atoms, N(1), N(2), O(2), O(1), from the least-squares mean plane through them are –0.077(4), 0.036(3), –0.079(2), and 0.037(2) Å, respectively for complex **5** and –0.042(3), 0.089(3), –0.046(2), and 0.091(2), respectively for complex

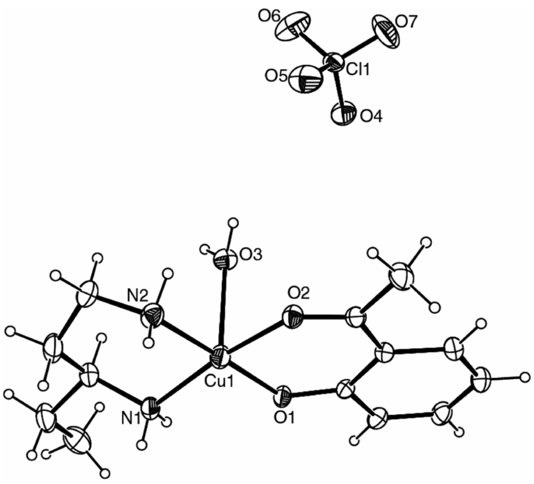


Figure 4. ORTEP-3 view of complex **5** with atom-numbering scheme (50% thermal ellipsoids).

Table 3. Selected bond lengths [Å] and bond angles [°] for complex **5** and **6**.

	5	**6**
Cu1–O1	1.910(2)	1.912(2)
Cu1–O2	1.954(2)	1.964(2)
Cu1–O3	2.369(2)	2.336(2)
Cu1–N1	2.006(3)	1.997(2)
Cu1–N2	1.993(3)	1.990(2)
O1–Cu1–O2	91.6(1)	91.1(1)
O2–Cu1–O3	85.6(1)	87.6(1)
O3–Cu1–N2	91.6(2)	90.7(1)
N1–Cu1–N2	92.2(1)	93.3(1)
O2–Cu1–N2	87.5(1)	87.9(1)
O1–Cu1–N1	88.3(1)	87.2(1)

Table 4. Hydrogen bond distances [Å] and angles [°] for the complexes **2**, **3**, **5**, and **6**.

	D–H···A	D–H	D···A	H···A	∠D–H···A
2	N2–H2b···O1^{i}	0.95(7)	2.964(6)	2.03(7)	171(6)
3	N23–H23a···O11^{j}	0.90(2)	3.057(4)	2.20(4)	158(3)
	N23–H23b···N3^{k}	0.90(2)	3.142(5)	2.29(3)	157(3)
5	N1–H1a···O5^{l}	0.80(6)	3.143(5)	2.43(7)	148(6)
	N2–H2b···O5^{m}	0.88(4)	3.177(5)	2.36(4)	156(4)
	O3–H3a···O1^{l}	0.86(2)	2.790(3)	1.94(2)	169(3)
	O3–H3b···O7^{m}	0.84(3)	2.949(5)	2.12(3)	168(6)
6	O3–H3a···O6^{n}	0.81(3)	2.811(4)	2.01(3)	171(3)
	O3–H3b···O1^{o}	0.72(4)	2.785(3)	2.08(4)	170(4)
	N1–H1a···O4^{p}	0.79(4)	3.283(4)	2.52(4)	162(3)
	N1–H1a···O5^{p}	0.79(4)	3.247(4)	2.57(3)	145(3)
	N2–H2a···O5^{n}	0.86(3)	3.095(4)	2.38(3)	141(3)
	N2–H2b···O6^{q}	0.88(4)	3.193(4)	2.51(3)	136(3)

Symmetry elements: (i) –1 + *x*, *y*, *z*; (j) 1 – *x*, 2 – *y*; 2 – *z*; (k) 2 – *x*, 2 – *y*, 2 – *z*; (l) 1 – *x*, – *y*, 1 – *z*; (m) –1/2 + *x*, 1/2 – *y*, –1/2 + *z*; (n) 1/2 – *x*, –1/2 + *y*, 1/2 – *z*; (o) 1 – *x*, –*y*, 1 – z; (p) *x*, –1 + *y*, *z*; (q) –*x*, 1 – *y*, –*z*.

6. The Cu atom is displaced from the mean plane by 0.084(4) Å and 0.093(3) Å towards the water molecule for complexes **5** and **6**, respectively. In both complexes the six-membered diamine chelate ring adopts chair conformation. The other chelate ring which is formed by the coordination of 2-hydroxyacetophenone to the metal centers is nearly planar with no atoms deviating from the least-squares mean plane by 0.039(4) Å and 0.012(3) Å for **5** and **6**, respectively.

Both the hydrogen atoms of the coordinated water molecule of the complexes are involved in hydrogen bonding (Table 4). One of the hydrogen atoms, H(3a) of **5** and H(3b) of **6** forms a strong hydrogen bond with the oxygen atom O(1)′ of the coordinated *o*-hydroxyacetophenone ligand of a centrosymmetrically related unit to form a hydrogen-bonded dimeric entity as shown in Figures 5 and S4 for complexes **5** and **6**, respectively. The other hydrogen atom of the water molecule, H(3b) of **5** and H(3a) of **6** is involved in a strong hydrogen-bonding interaction with one of the oxygen atoms [O(7) for **5** and O(6) for **6**] of the respective counteranions. The oxygen atoms of the corresponding counteranions [O(5) of ClO_4^- for **5** and O(4), O(5) of NO_3^- for **6**] act as a weak hydrogen-bond acceptor for the amine hydrogen H(1a) and H(2b) of **5** and the three amine hydrogen atoms [H(1a), H(2a), and H(2b)] of **6** to link the dimers and form two-dimensional net-like open framework structures of complexes **5** and **6** as shown in Figures 6 and S5, respectively.

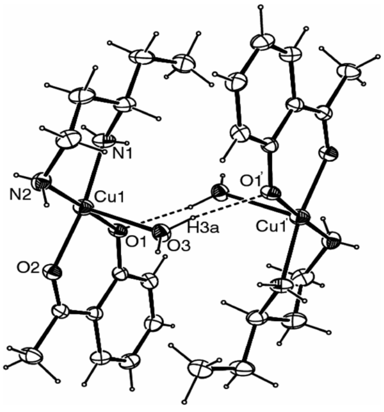


Figure 5. ORTEP-3 view of the hydrogen-bonded dimeric unit of **5** with atom-numbering scheme (25% thermal ellipsoids); atoms marked with (′) are transformed by the symmetry element 1 – *x*, –*y*, 1 – *z*.

Figure 6. Extended hydrogen-bonding network of complex **5**; the intermolecular hydrogen bonds are shown as dashed lines; atoms marked with (′) and (′′) are transformed by the symmetry element 1 – *x*, –*y*, 1 – *z* and –1/2 + *x*, 1/2 – *y*, –1/2 + *z*, respectively.

Complex 7

The structure of **7** is shown in Figure 7 together with the numbering scheme in the metal coordination spheres. The asymmetric unit of the complex contains 1.5 molecules of $Ni(hap)_2$, one (Ni1) in a general position and the other (Ni2) situated on a center of symmetry. Both molecules are square planar, and the metal atom is bonded to four oxygen atoms from two bidentate *o*-hydroxyacetophenone ligands in the equatorial plane. Bond lengths range from 1.832(3) to 1.861(3) Å (Table 5). The distances between Ni^{II} and the phenoxy O atom is shorter than that between the Ni^{II} atom and the ketone O atom as is usual for this type of complex.[18] Around Ni1, the average *trans* angle (178.6°) and

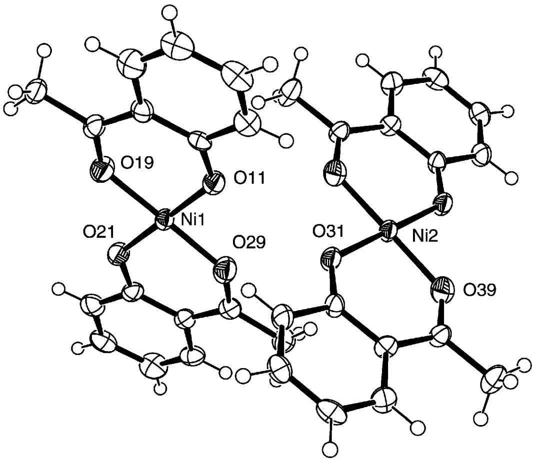


Figure 7. ORTEP-3 view of complex **7** with atom-numbering scheme (50% thermal ellipsoids).

Table 5. Selected bond lengths [Å] and bond angles [°] for complex **7**.

Ni(1)–O(11)	1.836(3)	Ni(2)–O(31)	1.833(3)
Ni(1)–O(21)	1.832(3)	Ni(2)–O(39)	1.854(3)
Ni(1)–O(29)	1.855(3)		
Ni(1)–O(19)	1.861(3)	O(31)–Ni(2)–O(39)	94.1(1)
O(11)–Ni(1)–O(21)	178.9(1)		
O(11)–Ni(1)–O(29)	86.3(1)		
O(21)–Ni(1)–O(29)	93.6(1)		
O(11)–Ni(1)–O(19)	93.3(1)		
O(21)–Ni(1)–O(19)	86.9(1)		
O(29)–Ni(1)–O(19)	178.2(2)		

the dihedral angle between the two O–Ni–O planes (1.69°) indicate a slight tetrahedral distortion from a perfectly square-planar arrangement.

Conclusions

In the present study, it has been shown that a mono-condensed Schiff base of 1,3-pentanediamine and *o*-hydroxyacetophenone can conveniently be synthesized as a bis-chelate octahedral Ni^{II} complex. However, a similar bis-chelate complex of 1,2-ethanediamine and its derivative can not be synthesized by using the same procedure; instead a square planar di-Schiff base complex of Ni^{II} results presumably due to its stronger ligand field strength. Here we also illustrate that the counteranions of the metal salt play a very important role in the stability and hydrolysis of the Schiff base during complex formation. The observations have been rationalized by an anion-directed cation templating effect. When one of the four coordination sites of the square plane of the metal ion is occupied by a strongly coordinating anion, the tridentate mono-Schiff base is stabilized through coordination to the three remaining sites. However, with weakly coordinating counteranions, all four equatorial sites of Cu^{II}/Ni^{II} are to be coordinated preferably by strong-field ligands, and this requirement is fulfilled by the hydrolytic cleavage of the tridentate Schiff base. The possibility of the presence of equilibrium which may shift during the crystallization toward the less soluble species may also be imperative for isolation of complexes in the solid state.

Experimental Section

Starting Materials: All the chemicals were of reagent grade and were used without further purification.

Physical Measurements: Elemental analysis (carbon, hydrogen, and nitrogen) was performed with a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded with a Perkin–Elmer RXI FT-IR spectrophotometer. The electronic absorption spectra (1200–350 nm) in acetonitrile solution and solid-state reflectance spectra of the complexes were recorded with a Hitachi U-3501 spectrophotometer. The thermal analyses (TGA-DTA) were carried out with a Mettler Toledo TGA/DTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 $cm^3 min^{-1}$). The samples were heated in an alumina crucible at a rate of 10 °C min^{-1}. Cyclic voltammetry was carried out using the Sycopel model AEW2 1820F/S instrument. The measurements were performed at 300 K by using TEAP (0.2 M) as the supporting electrolyte and Ni^{II} (10^{-3} M) and Cu^{II} (10^{-3} M) complexes deoxygenated by bubbling with nitrogen. The working, counter-, and reference electrodes used were a platinum wire, a platinum coil, and an SCE, respectively. The ^1H NMR spectra at 300 MHz were recorded in $CDCl_3$ with a Bruker AV 300 Spectrometer.

Synthesis of the Complex $[NiL_2]·2H_2O$ (1): This compound was prepared by following the method reported by Elder.[10] Briefly, bis(*o*-hydroxyacetophenone)nickel(II) dihydrate (3.37 g, 10 mmol) was slurried in absolute ethanol (30 mL), and 1,3-pentanediamine (2.98 mL, 25 mmol) was added to it. The green slurry quickly dissolved to give a brown solution from which the green-brown solid subsequently separated. The mixture was heated at reflux for 2 h. Ethanol (50 mL) was added to dissolve all solids. The solution, filtered hot and cooled to –10 °C, deposited yellow-gold needle crystals. On exhaustive washing with acetone, the compound appeared as a straw-colored finely crystalline solid.

Complex 1: Yield 3.72 g (75%). $C_{26}H_{42}N_4NiO_4$ (533.3): calcd. C 58.55, H 7.94, N 10.51; found C 58.42, H 7.87, N 10.36. UV/Vis (solid, reflectance): λ_{max} = 561 and 980 nm. IR: ν(N–H) = 3344 and 3205, ν(C=N) = 1612 , ν(O–H) = 3434 cm^{-1}.

Preparation of the Ligand 2-[1-(3-Aminopentylimino)ethyl]phenol (HL): A solution of the ligand (10 mmol) was obtained by heating at reflux the Ni^{II} complex (**1**) (2.49 g, 5 mmol) with dimethylglyoxime (H_2DMG) (2 equiv., 1.16 g, 10 mmol) in methanol (20 mL) for 2 h and filtering the precipitate of $Ni(DMG)_2$ according to the procedure of Burke and McMillin.[11] The solvent was removed from the filtrate by rotary evaporation to leave a yellow oil.

HL: $C_{13}H_{20}N_2O$ (220.30): calcd. C 70.87, H 9.15, N 12.72; found C 70.67, H 9.04, N 12.56. ^1H NMR (300 MHz, 20 °C, $CDCl_3$): δ = 0.876–0.905 (t, 3 H, 13-H), 1.322–1.491 (m, 2 H, 12-H), 2.817–2.991 (m, 1 H, 11-H), 1.754–1.888 (m, 2 H, 10-H), 3.638 3.685 (t, 2 H, 9-H), 0.915 (s, 3 H, 8-H), 5.153 [broad, 2 H, $H(NH_2)$], 6.722 (d, 1 H, 2-H), 7.1521.232 (m, 1 H, 3-H), 6.746–6.790 (m, 1 H, 4-H), 7.492 (d, 1 H, 5-H) ppm.

Synthesis of the Complex [NiL(NCS)] (2): $Ni(NCS)_2·4H_2O$ (1.24 g, 5.0 mmol), dissolved in hot methanol (10 mL), was added to a methanol solution (10 mL) of the ligand (HL) (5.0 mmol) and stirred for ca. 10 min. The color of the solution turned to light green. The filtrate was left to stand overnight in air, then dark red X-ray quality single crystals of complex **2** appeared at the bottom of the vessel on slow evaporation of the solvent.

Complex 2: Yield 1.34 g (80%). $C_{14}H_{19}N_3NiOS$ (336.08): calcd. C 50.03, H 5.70, N 12.50; found C 50.12, H 5.67, N 12.36. UV/Vis (solid, reflectance): λ_{max} = 474 nm. IR: ν(N–H) = 3205 and 3084, ν(C=N) = 1596, ν(SCN) = 2093 cm^{-1}.

Synthesis of the Complex $[CuL(N_3)]_2$ (3): A solution of $CuCl_2·2H_2O$ (0.85 g, 5 mmol) in methanol (10 mL) was mixed with the ligand HL (5 mmol) in methanol (10 mL) with constant stirring. After ca. 15 min, a methanol/water solution (9:1, v/v) of NaN_3 (0.32 g, 5 mmol) was added, and stirring was continued for ca. 15 min. Upon stirring a green precipitate separated out. It was dissolved in MeCN and was filtered. Upon slow concentration of the resulting solution, dark green single crystals of **3** suitable for X-ray diffraction analysis were obtained.

Complex 3: Yield 1.37 g. (85%). $C_{26}H_{38}Cu_2N_{10}O_2$ (649.76): calcd. C 48.06, H 5.89, N 21.56; found C 48.10, H 5.72, N 21.75. UV/Vis (solid, reflectance): λ_{max} = 602 nm. IR: ν(N–H) = 3261, 3203 and 3128, ν(C=N) = 1589, ν(N_3^-) = 2043 cm^{-1}.

Synthesis of the Complex [CuL(NCS)] (4): A solution of $CuCl_2·2H_2O$ (0.85 g, 5 mmol) in methanol (10 mL) was mixed with the ligand, HL (5 mmol) in methanol (10 mL) with constant stirring. After ca. 15 min a methanol/water solution (9:1, v/v) of NH_4SCN (0.38 g, 5 mmol) was added, and stirring was continued for ca. 15 min when a brown precipitate separated out. The precipitate was filtered, washed with methanol and dried in air.

Complex 4: 1.36 g (80%). $C_{14}H_{19}CuN_3OS$ (340.06): calcd. C 49.32, H 5.62, N 12.33; found C 49.10, H 5.59, N 12.45. UV/Vis (solid, reflectance): λ_{max} = 379, 586 nm. IR: ν(N–H) = 3208 and 3148, ν(C=N) = 1591, ν(SCN^-) = 2104 cm^{-1}.

Table 6. Crystal data and structure refinement of complexes **2**, **3**, **5**, **6**, and **7**.

	2	**3**	**5**	**6**	**7**
Formula	$C_{14}H_{19}N_3NiOS$	$C_{26}H_{38}Cu_2N_{10}O_2$	$C_{13}H_{23}ClCuN_2O_7$	$C_{13}H_{23}CuN_3O_6$	$C_{16}H_{14}NiO_4$
M	336.09	649.76	418.33	380.89	328.98
Space group	$P2_12_12_1$	$P\bar{1}$	$P21/n$	$P21/n$	$P\bar{1}$
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	triclinic
a [Å]	5.440(3)	7.3798(6)	9.435(3)	9.555(3)	9.110(1)
b [Å]	13.111(3)	9.2805(8)	16.341(3)	15.917(3)	11.340(1)
c [Å]	21.284(3)	10.6565(8)	11.878(2)	11.613(2)	11.785(1)
α [°]	90	88.099(7)	90	90	100.85(9)
β [°]	90	83.037(6)	105.14(2)	106.61(3)	93.46(9)
γ [°]	90	84.308(7)	90	90	109.63(1)
V [Å^3]	1518.1(9)	720.73(10)	1767.8(7)	1692.5(7)	1116.2(2)
Z	4	1	4	4	3
$D_{\text{calcd.}}$ [g cm^{-3}]	1.470	1.497	1.572	1.495	1.468
μ [mm^{-1}]	1.414 (Mo-K_α)	1.518 (Mo-K_α)	3.477 (Cu-K_α)	1.323 (Mo-K_α)	1.315 (Mo-K_α)
R(int.)	0.077	0.034	0.012	0.035	0.033
No. of unique data	3372	3981	3331	4199	6100
No. of data with $I > 2\sigma(I)$	2326	2163	3020	3038	4105
$R1$, $wR2$	0.0563, 0.1347	0.0550, 0.1278	0.0459, 0.1413	0.0385, 0.1155	0.0724, 0.1656

Synthesis of the Complexes [Cu(hap)(pn)(H_2O)]ClO_4 (5) and [Cu(hap)(pn)(H_2O)]NO_3 (6): A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.85 g, 5 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (1.21 g, 5 mmol) in methanol (10 mL) was added to a solution of HL (1.095 g, 5.0 mmol) in methanol (10 mL) separately with constant stirring. Unlike **3** and **4** no immediate separation of solid product took place for these compounds. Instead, on keeping the resulting solution in an open atmosphere for ca. 24 h, the respective ternary complexes **5** and **6** separated as dark green block-shaped single crystals suitable for X-ray analysis.

Complex 5: Yield 1.25 g (60 %). $C_{13}H_{23}ClCuN_2O_7$ (418.33): calcd. C 37.32, H 5.54, N 6.70; found C 37.12, H 5.67, N 6.54. UV/Vis (solid, reflectance): $\lambda_{\max}$ = 594 nm. IR: ν(N–H) = 3328 and 3263, ν(C=O) = 1612, ν(H_2O) = 3508, ν(ClO_4^-) = 1088 (ν_3) and 948 cm^{-1} (ν_4).

Complex 6: Yield 1.24 g (65 %). $C_{13}H_{23}CuN_3O_6$ (380.50): calcd. C 40.99, H 6.09, N 11.03; found C 40.82, H 5.97, N 10.86. UV/Vis (solid, reflectance): $\lambda_{\max}$ = 595 nm. IR: ν(N–H) = 3232 and 3148, ν(C=O) = 1612, ν(H_2O) = 3508, ν(NO_3^-) = 1434 (ν_5), 1375 (ν_1) and 1032 cm^{-1} (ν_2),

Synthesis of the Complexes [Ni(hap)$_2$] (7): A solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (1.83 g, 5 mmol) or $Ni(NO_3)_2{\cdot}6H_2O$ (1.46 g, 5 mmol) in methanol (10 mL) was added to a solution of HL (1.095 g, 5.0 mmol) in methanol (10 mL) with constant stirring; immediate separation of red solid took place. The solid was dissolved in CH_2Cl_2 and was filtered. Upon slow concentration of the resulting solution, dark red single crystals of **7**, suitable for X-ray diffraction analysis were obtained.

Complex 7: Yield 0.66 g (40 %). $C_{16}H_{14}NiO_4$ (328.96): calcd. C 58.42, H 4.29; found C 58.34, H 4.37. UV/Vis (solid, reflectance): $\lambda_{\max}$ = 458 nm. IR: ν(C=O) = 1571, ν(C–O) = 1240 cm^{-1}

Crystallographic Studies: The data for complexes **2** and **6** were collected at room temperature with Mo-K_α radiation by using a Bruker AXS Smart single crystal diffractometer with CCD (area detector). The absorption correction was performed with the method inserted in SHELXTL-NT V5.1.[23] The structure was solved by direct methods with the software SHELXTL-NT V5.1 inserted in the Bruker AXS software.[23]

For complex **3** and **7**, the data were collected with Mo-K_α radiation by using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analysis was carried out with the Crysalis program.[24] The structure was solved by direct methods with the SHELXL97 program.[25] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program.[26] The structures were refined on F^2 using SHELXL97[25] to $R1$ 0.0550 and 0.0724, $wR2$ 0.1117 and 0.1656 for 2163 and 4105 reflections with $I > 2\sigma(I)$ for complexes **3** and **7**, respectively.

The data of **5** were collected at room temperature with Cu-K_α radiation with a Siemens AED single crystal diffractometer with a local program.[27] The preliminary cell parameters were obtained from the least-squares analysis of the (θ,χ,ϕ) angular values of 3331 reflections (θ range: 4–70°) accurately centered on the diffractometer. The intensity of one standard reflection, recorded for every 100 reflections, showed no significant changes. The recorded data were corrected for polarization and Lorentz effects. The absorption correction was performed by the method of Walker and Stuart[28] with a program written by Gluzinski.[29]

In complexes **2**, **5**, and **6**, the non-hydrogen atoms were refined anisotropically while the hydrogen atoms, either located from difference electron density maps or placed geometrically, were refined with isotropic thermal parameters. Neutral atom scattering factors were taken from Cromer and Weber[30] and anomalous dispersion effects were included in $F_{\text{calcd.}}$[31] The crystallographic illustrations were prepared using ORTEP-3.[32] Details of crystallographic data and refinements of the complexes are summarized in Table 6, while selected bond lengths and bond angles are presented in Tables 1, 2, 3, and 5. A list of hydrogen bonds in the complexes is given in Table 4.

Crystallographic data in CIF format for the structures are reported. CCDC-677887 (for **2**), -677888 (for **3**), -677889 (for **5**), -677890 (for **6**), and -685126 (for **7**) 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 footnote on the first page of this article): Figures of hydrogen-bonded 1D chain of complex **2**, hydrogen-bonded 1D chain of complex **3**, ORTEP-3 view of complex **6**, ORTEP-3 view of the hydrogen-bonded dimeric units of complex **6**, extended hydrogen-bonding network of complex **6**.

Acknowledgments

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