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Complexing Properties of *Schiff* Bases with Copper and Nickel Ions

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Summary. The solution properties of *PPP*, *QPP*, and their complexes with copper and nickel were investigated. The composition and stability of the complexes have been determined using the spectrophotometric method at $T = 25 \pm 1$ °C, constant ionic strength ($I = 0.5\,M$, adjusted with KNO_3) and a volume ratio of methanol/water of $\varphi = 0.10$ and 0.16 for *PPP* and *QPP*, respectively, due to lower solubility of *QPP*. The experimental results have been fitted to the theoretical equations using the computerized iterative method of successive approximation. The influence of *pH* and addition of another benzene ring to the ligand molecule has been studied. The structures of isolated solid metal complexes with *QPP* were investigated by infrared and mass spectroscopy. The use of *PPP* and *QPP* as analytical reagents for spectrophotometric determinations of copper and nickel is discussed.

Keywords. *Schiff* base; 4-(2-Pyridylmethylene)-amino-1-phenyl-2,3-dimethyl-5-pyrazolone; 4-(2-Quinolylmethyleneamino)-1-phenyl-2,3-dimethyl-5-pyrazolone; Copper; Nickel; Spectroscopic investigations.

Komplexbildende Eigenschaften von *Schiff*schen Basen mit Kupfer- und Nickelionen

Zusammenfassung. Die Eigenschaften von *PPP*, *QPP* und ihrer Komplexe mit Kupfer und Nickel in Lösung wurden untersucht. Zusammensetzung und Stabilität der Komplexe wurde bei 25 ± 1 °C, konstanter Ionenstärke ($I = 0.5\,M$, eingestellt mit KNO_3) und einem. Methanol/Wasser–Volumenverhältnis von $\varphi = 0.10$ und 0.16 für *PPP* bzw. *QPP* (bedingt durch die geringere Löslichkeit von *QPP*) bestimmt. Die experimentellen Ergebnisse wurden mittels eines Algorithmus zur sukzessiven Approximation an die theoretischen Gleichungen angepaßt. Der Einfluß des *pH*-Werts und eines weiteren aromatischen Rings am Liganden wurden studiert. Die Strukturen der isolierten festen Komplexe mit *QPP* wurden mittels IR- und Massenspektroskopie untersucht. Die Verwendung von *PPP* und *QPP* als analytische Reagenzien zur spektrophotometrischen Bestimmung von Kupfer und Nickel wird diskutiert.

Introduction

Azomethine compounds prepared from 4-aminoantipyrine and 2-pyridinecarbaldehyde or 2-quinolylcarbaldehyde are interesting from several points of view. As *Schiff* bases with O and N donor atoms they might be potential ligands for the analytical determination of transition metal ions [1–6]. Isolated in solid state as ligands or metal complexes, they can be used as pigments and dyes in textile industry [7–9]. Finally, as pharmaceuticals, these azomethines and their homologes have much better antiinflammatory activity against carrageenan edema, and lower toxicity, compared to that of the starting amines [10].

The synthesis of 4-(2-pyridylmethylene)-amino-1-phenyl-2,3-dimethyl-5-pyrazolone (*PPP*) and 4-(2-quinolylmethyleneamino)-1-phenyl-2,3-dimethyl-5-pyrazolone (*QPP*) and their copper and nickel complexes were reported earlier [11, 12], but only the nature of bonding in metal complexes with *PMAP* has been studied and established by means of elemental analysis, IR and mass spectrometry. The analyses of data showed that both isolated solid complexes of copper and nickel with *PMAP* have a metal-to-ligand ratio 1:2 and a ionic molecular structure with perchlorate as an anion. The solution properties, except the solubility in different solvents, were not investigated.

The aim of this work was to investigate the solution properties of both ligands, *PPP* and *QPP*, and their complexes with copper and nickel, at different *pH* values. The influence of the addition of another benzene ring on stability and complexing properties has been discussed. A detailed study of IR and mass spectra for *QPP*, Ni–*QPP*, and Cu–*QPP* and the possibility of using *PPP* and *QPP* as spectrophotometric reagents for the determination of copper and nickel is presented.

Results and Discussion

The isolated bright yellow crystals of the *QPP* and Ni–*QPP* complexes and the dark brown-red crystals of the Cu–*QPP* complex were characterized by solubility measurements, IR and mass spectroscopy.

Solubility

The solubilities of *QPP* and the Cu–*QPP* and Ni–*QPP* complexes in different solvents are presented in Table 1. Comparing the solubility of *QPP* and *PPP* [11], it is obvious that the addition of another benzene ring lowers the solubility in more polar solvents. Different solvents, in respect of their increasing polarity, cause a bathochromic shift in solutions of Cu–*QPP* complexes. Changing the solvent from benzene to *DMF*, a positive solvatochromism occurs. An exception is the very pale yellow colour of the complex dissolved in water, which is most likely due to its very low solubility. Better solubility of metal complexes in polar than in nonpolar solvents confirms their ionic strucutre. This is in good agreement with elemental analyses data [12].

Infrared Spectroscopy

The assignments of some important bands of the ligand and its metal complexes are presented in Table 2. In the spectra of *QPP*, the ν(C=O) frequencies were found at $1650\,\mathrm{cm}^{-1}$. In the spectra of the metal complexes this band is shifted to lower frequencies: for Ni–*QPP* to $1630\,\mathrm{cm}^{-1}$, while for Cu–*QPP* it overlaps with the ν(C=N) band. These shifts of ν(C=O) frequencies in both complexes to lower wave numbers indicate that the carbonyl oxygen atom is involved in bonding to the metal atom. This fact is further supported by the appearance of a strong band at 390 and $375\,\mathrm{cm}^{-1}$ (M–O bonding).

Table 1. Solubility of *QPP* and its metal complexes in different solvents

Solvent	*QPP* solubility Cold	*QPP* solubility Warm	Colour	Cu–*QPP* solubility Cold	Cu–*QPP* solubility Warm	Colour	Ni–*QPP* solubility Cold	Ni–*QPP* solubility Warm	Colour
Water	–	–		–	+ –	Bright yellow	+ –	+ –	Bright yellow
Ethanol	+ –	+ +	Yellow	+	+ +	Orange yellow	+ –	+ –	Bright yellow
Methanol	+ –	+ +	Green yellow	+	+ +	Orange yellow	+ –	+ –	Bright yellow
Acetone	+ –	+ +	Green yellow	+	+ +	Orange yellow	+ –	+	Dark yellow
DMF	+ –	+ +	Orange red	+ +	+ +	Orange red	+ +	+ +	Dark yellow
Pethrolether	–	–		–	–		–	–	
Benzene	+ –	+ –	Yellow	–	–		+ –	+ –	Dark yellow
Chloroform	+ –	+	Green yellow	+ –	+	Yellow	+ –	+ –	Yellow
Pyridine	+ +	+ +	Dark yellow	+ +	+ +	Yellow	+ +	+ +	Dark yellow
Acetic acid	+ +	+ +	Orange red	+ +	+ +	Orange red	+ +	+ +	Yellow
Sulphuric acid	+	+ +	Orange red	+ +	+ +	Yellow	+ +	+ +	Yellow

–: insoluble; + –: slightly soluble; +: soluble; + +: very soluble

The ν(C=N) frequencies in *QPP* occur at 1615, 1595, and 1570 cm^{-1}. In the spectra of Cu–*QPP* and Ni–*QPP*, slight shifts of these frequencies and changes in abundance of bands were observed. The appearance of bands at 530, 505, 495, 480, and 415 cm^{-1} in the spectra of the metal complexes suggests the presence of M–N bonding.

Table 2. Infrared wave numbers in cm^{-1} and assignments for *QPP*, Cu–*QPP* and Ni–*QPP* in the range from 3600–370 cm^{-1}

QPP	Cu–*QPP*	Ni–*QPP*	Assignment
	3440 (w)	3420 (w)	ν(OH)
3040 (w)	3040 (w)	3040 (w)	ν(C–H) aromatic
1650 (s)		1630 (m)	ν(C=O)
1615 (w)	1620 (s)	1615 (m)	
1595 (m)	1595 (w)	1600 (m)	ν(C=N)
1570 (m)		1580 (s)	
1480 (m)	1490 (s)	1500 (s)	δ(=CH) phenyl, in plane
1455 (w)	1450 (w)	1455 (w)	δ(–CH$_3$) assymmetric
1415 (m)	1410 (m)	1430 (m)	
1375 (w)	1350 (w)	1380 (s)	δ(–CH$_3$) symmetric
1355 (w)			
1320 (w)	1325 (w)		ν(C–N)
1300 (m)	1305 (w)	1305 (m)	
1220 (w)	1220 (w)	1230 (m)	ν(C–N) quinoline
1130 (m)	1040 (w)	1040 (w)	δ(C–C)
1110 (w)	1020 (w)		
	1090 (s)	1090 (s)	ν(Cl–O) perchlorate
955 (m)	950 (w)	985 (m)	δ(C–H) aromatic, in plane
		930 (m)	
890 (w)	870 (w)	870 (w)	
860 (m)	840 (w)	830 (m)	
830 (s)	780 (w)	805 (m)	
780 (w)	760 (m)	785 (w)	δ(C–H) aromatic, out of plane
760 (s)	700 (m)	775 (w)	
745 (m)	670 (w)	760 (s)	
695 (s)		700 (s)	
		690 (w)	
		675 (w)	
	630 (w)	630 (w)	ν(Cl–O) perchlorate
	530 (w)	530 (w)	ν(*M*–N)
	505 (m)	505 (w)	
	480 (m)	495 (w)	
	415 (m)	415 (m)	
	390 (m)	390 (m)	ν(*M*–O)
	375 (s)	375 (s)	

Abbreviations: *M* metal (Cu, Ni); s strong; m medium; w weak; Assignments: ν vibrational; δ bending deformation

A weak band at $1220\,\mathrm{cm}^{-1}$ in the spectra of *QPP* and Cu–*QPP* corresponds to C–N stretching vibrations of the quinoline ring. In the spectra of Ni–*QPP*, the C–N band occurs at higher wave numbers ($1230\,\mathrm{cm}^{-1}$) and changes its abundance. Therefore, the involvement of the N atom in bonding is confirmed only for the Ni–*QPP* complex.

The OH stretching vibrations at $3440\,\mathrm{cm}^{-1}$ and $3420\,\mathrm{cm}^{-1}$ in the spectra of Cu–*QPP* and Ni–*QPP* suggest the presence of a water molecule, and the broad band at $1090\,\mathrm{cm}^{-1}$, as well as a sharp band at $630\,\mathrm{cm}^{-1}$, indicates the presence of the perchlorate ion.

The characteristic bands for the phenyl group at $1480–1500\,\mathrm{cm}^{-1}$ and for the methyl group at $1455–1410\,\mathrm{cm}^{-1}$ and $1380–1350\,\mathrm{cm}^{-1}$ are also observed. These substituents on 5-pyrazolone, phenyl at position 1 and two methyl groups at positions 2 and 3, enable pyrazolone to exist only in the keto form which is confirmed by the ν(C=O) frequencies found in the spectra of all compounds.

Mass Spectroscopy

The mass spectrum of *QPP* shows a well defined parent peak at $m/z = 342$. The $C_3H_4O^+$ ion, $m/z = 56$, is the base peak in the spectrum of the ligand. The parent ion fragments by cleavage in quinoline ($m/z = 155$) and pyrazolone ($m/z = 187$). The recombination of quinoline and pyrazolone fragments and their possible cleavage is shown in the mass histogram of *QPP* (Fig. 1).

The structures of Cu–*QPP* and Ni–*QPP* are shown in Fig. 2. As these complexes are large molecules, it is difficult to obtain the parent peak in their mass spectra. Although the parent ions are not observed in the mass spectra of Cu–*QPP* and Ni–*QPP*, the existence of two ligands in the molecules could be established. The spectra of the complexes are similar with base peaks at $m/z = 484$, which implies that the loss of the metal ion is the first step of the fragmentation. It can be supposed that some combinations of fragments occur after elimination of the metal ion. Some proposed combinations are shown in Figs. 1 and 2.

Compiling all results obtained by solubility measurements, IR and mass spectroscopy, the structure of copper and nickel complexes with *QPP* can be proposed

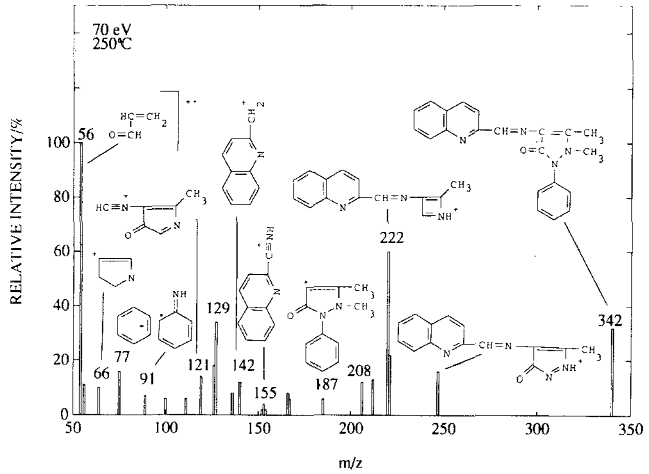

Fig. 1. Mass histogram of *QPP*

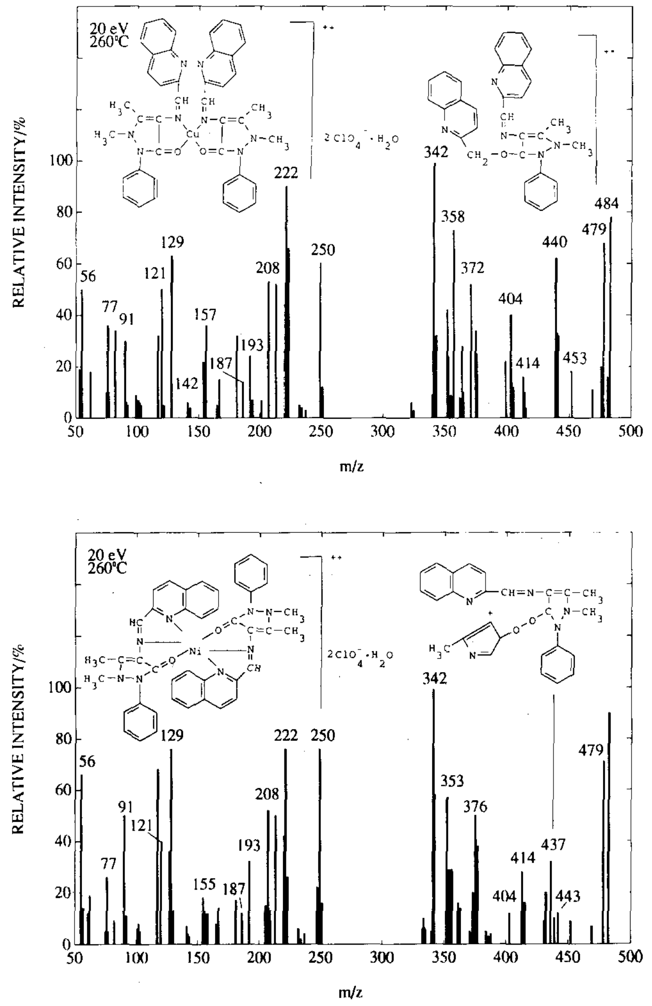

Fig. 2. Mass histograms of (A) Cu–*QPP* and (B) Ni–*QPP*

(Fig. 2). Both metal ions are bound to two *QPP* ligands giving a ionic molecular structure with two perchlorates as anions and one molecule of water in the outer sphere of the molecule.

UV/Vis Spectroscopy

The solution properties of *PPP* and *QPP* have been investigated in methanol/water at a temperature of 25 ± 1 °C and at constant ionic strength ($I = 0.5\,M$, adjusted with KNO$_3$). Due to the lower solubility of *QPP* it was necessary to increase the volume ratio of methanol/water from $\varphi = 0.10$ for *PPP* to $\varphi = 0.16$ for *QPP*. Results given in Fig. 3 show that the absorbance of both ligands is strongly influenced by the change in *pH* of the solution. The highest value is obtained in unbuffered solutions. At low *pH* values, the π system of pyridine is distorted due to the protonation of the N atom in pyridine which implies a hypsochromic shift of absorption maxima. When the *pH* is changed from 3 to 5 in the solutions of *PPP*, a hypsochromic shift of absorption maxima ($\Delta\lambda = 110\,\text{nm}$) is observed. At low *pH*

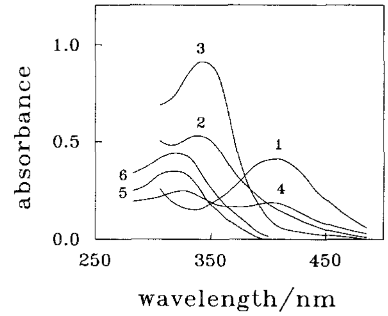

Fig. 3. Absorption spectra of *PPP* and *QPP* at different *pH* values and $t = 10\,\mathrm{min}$. *PPP*: $\varphi(CH_3OH) = 0.1$; $c(PPP) = 0.2\,\mathrm{m}M$; (1) $pH = 3$; (2) $pH = 5$; (3) no buffer. *QPP*: $\varphi(CH_3OH) = 0.16$; $c(QPP) = 0.1\,\mathrm{m}M$; (4) $pH = 3$; (5) $pH = 5$; (6) no buffer

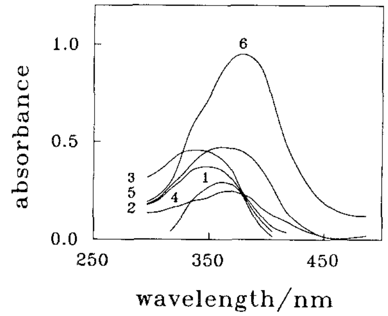

Fig. 4. Absorption spectra of Cu–*PPP* and Cu–*QPP* at different *pH* values and $t = 10\,\mathrm{min}$; $c(\mathrm{ligand}) = 0.2\,\mathrm{m}M$; $c(\mathrm{Cu}) = 0.02\,\mathrm{m}M$ (except for Cu–*PPP* at $pH = 3$ where $c(\mathrm{Cu}) = 0.08\,\mathrm{m}M$). Cu–*PPP*: $\varphi(CH_3OH) = 0.1$; (1) $pH = 3$; (2) $pH = 5$; (3) no buffer; Cu–*QPP*: $\varphi(CH_3OH) = 0.16$; (4) $pH = 3$; (5) $pH = 5$; (6) no buffer

($pH = 3$), *QPP* has two absorption maxima at $\lambda = 320$ and 410 nm, while at higher *pH* values only the maximum at 320 nm can be observed.

Addition of another benzene ring usually causes a bathochromic shift in absorption spectra. However, the results presented in Fig. 3 show a hypsochromic shift. The reason might be the lower solubility of *QPP*, as a consequence of which the volume ratio of methanol/water had to be increased and, as was experimentally confirmed, the increase of the methanol fraction in the solvent mixture causes a hypsochromic shift. Molar absorption coefficients are higher for *QPP* than for *PPP*, the difference being less pronounced in unbuffered solutions.

The absorption spectra of Cu–*PPP* and Cu–*QPP* measured against reagent blank show the hypsochromic and hyperchromic effects with increasing *pH* (Fig. 4). The wavelength of absorption maxima changes from $\lambda = 360\,\mathrm{nm}$ ($pH = 3$; curve 1) to $\lambda = 340\,\mathrm{nm}$ (unbuffered solution; curve 3) for Cu–*PPP* and $\lambda = 365\,\mathrm{nm}$ ($pH = 3$; curve 4) to $\lambda = 355\,\mathrm{nm}$ ($pH = 5$; curve 5) for Cu–*QPP* which exhibit a bathochromic shift of $\Delta\lambda = 25\,\mathrm{nm}$ with further increase of *pH* (unbuffered solution; curve 6). Comparing the molar absorption coefficients of Cu–*PPP* and Cu–*QPP*, it can be seen that the chromophoric properties of the *QPP* complex are enhanced.

The absorption spectra of Ni–*PPP* and Ni–*QPP* in solution are influenced by *pH* as well (Fig. 5). The highest value of absorbance is obtained in unbuffered solutions. Two absorption maxima at $\lambda = 380\,\mathrm{nm}$ and $\lambda = 430\,\mathrm{nm}$ are obtained at $pH = 3$ for Ni–*QPP* which suggests that at this *pH* different complex species exist. The color of complexes with both ligands developed completely after 10 min.

Determination of Stability Constants

The composition and stability constants of Ni(II) and Cu(II) complexes of *PPP* and *QPP* were determined *via* a computerized version of mole ratio method [13], which

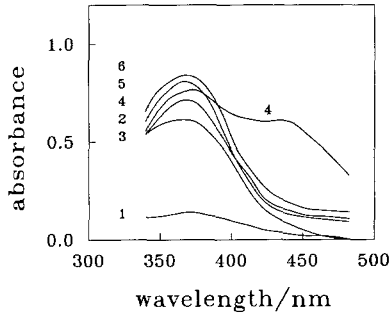

Fig. 5. Absorption spectra of Ni–*PPP* and Ni–*QPP* at different *pH* values and $t = 10\,\text{min}$. Ni–*PPP*: $\varphi(CH_3OH) = 0.1$; $c(PPP) = 0.2\,\text{m}M$; $c(\text{Ni}) = 0.08\,\text{m}M$; (1) $pH = 3$; (2) $pH = 5$; (3) no buffer. Ni–*QPP*: $\varphi(CH_3OH) = 0.16$; $c(QPP) = 0.2\,\text{m}M$; $c(\text{Ni}) = 0.04\,\text{m}M$; (4) $pH = 3$; (5) $pH = 5$; (6) no buffer

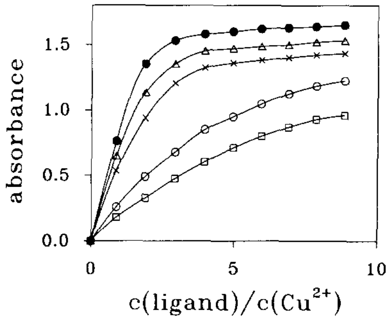

Fig. 6. Absorption *vs.* metal-to-ligand mole ratio curves for Cu–*PPP* and Cu–*QPP*; $c(\text{Cu}) = 0.1\,\text{m}M$; Cu–*PPP*: ●: $pH = 3$; ×: no buffer; Cu–*QPP*: △: $pH = 3$; *: $pH = 5$; ○: no buffer

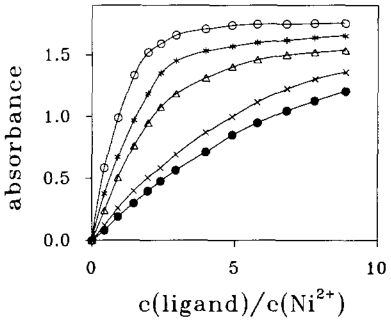

Fig. 7. Absorption *vs.* metal-to-ligand mole ratio curves for Ni–*PPP* and Ni–*QPP*; $c(\text{Ni}) = 0.1\,\text{m}M$; Ni–*PPP*: □: $pH = 5$; ○ no buffer; Ni–*QPP*: ×: $pH = 3$; △: $pH = 5$; ●: no buffer

is based on a successive approximation calculation using the general equation valid for the method with the assumption of the existence of a single predominant complex species (Figs. 6 and 7). Stability constants of Ni(II) and Cu(II) complexes with *PPP* were determined also by the mole fraction variation method (*Job*'s method) using the computerized algorithm proposed by *W. Likussar et al.* [14–16] based on iterative successive approximation of the theoretical equation describing the absorbance *vs.* mole fraction curves (Fig. 8). Logarithmic values of the stability constants together with their relative standard errors obtained by these two methods are summarized in Table 3. Some discrepancies, however, have been obtained concerning the composition of the single predominant complex species present in the solution judged by the value of the relative standard errors obtained. The mole fraction variation method for Ni–*PPP* suggests that ML_2 or even higher complex species are present in the solution. The mole ratio method is favoring ML_2 complex

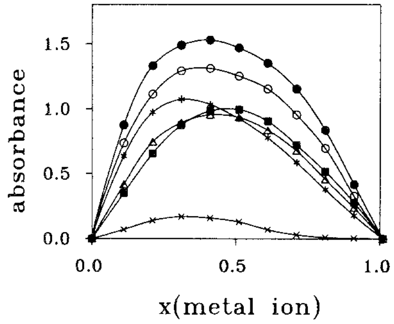

Fig. 8. Absorption *vs.* metal ion mole fraction curves for Ni–*PPP* and Cu–*PPP* complexes; Ni–*PPP*: × :$pH = 3$; △: $pH = 5$; ∗: no buffer; Cu–*PPP*: ■: $pH = 3$; ○: $pH = 5$; ●: no buffer

species, which is not surprising considering different experimental conditions used in these two methods. The highest values for stability constants for all metal complexes were obtained in unbuffered solutions, which means that in buffered solutions the mixed complex species might exist simultaneously. For Cu–*PPP*, both methods suggest that ML and ML_2 types of complex species are formed depending on the *pH* of the solution. It can be concluded that Ni(II) and Cu(II) give consecutive complexes with *PPP* simultaneously present in the solution; so the results obtained are only of approximate value.

The composition and stability of Ni(II) and Cu(II) complexes with *QPP* determined with mole ratio method clearly indicate that both metal ions form ML_2 type complex species with higher stability then those with *PPP*. For both ligands, Cu(II) complexes are more stable then Ni(II) complexes.

Table 3. Predominant composition and stability constants of Cu and Ni complexes with *PPP* and *QPP* determined by mole fraction variation (MFV) and mole ratio variation (MRV) at different *pH* values

			$\log\beta_i$		
	pH	*M*:*L*	MFV	*M*:*L*	MRV
Cu–*PPP*	3	1:1	3.92±0.08	1:2	9.05±0.09
	5	1:1	3.93±0.07		
	5	1:2	8.68±0.08		
	no buff.	1:2	8.70±0.06	1:1	4.11±0.11
				1:2	9.08±0.10
Ni–*PPP*	3	1:2	6.56±0.07		
	5	1:2	7.46±0.01	1:2	8.50±0.06
	no buff.	1:2	7.42±0.06	1:2	9.24±0.06
Cu–*QPP*	3			1:2	11.12±0.09
	5			1:2	11.42±0.08
	no buff.			1:2	11.86±0.02
Ni–*QPP*	3			1:2	8.93±0.07
	5			1:2	9.20±0.08
	no buff.			1:2	9.74±0.04

Application

The results obtained suggest that *PPP* and *QPP* can be used as possible spectrophotometric reagents for the determination of nickel and copper. The possibility of using these two azomethine ligands for the determination of nickel in real samples of bronzes has been investigated. Copper as a major component in bronzes is separated electrogravimetrically and can therefore not be determined. However, the possibility of copper determination was investigated as well, in order to enlarge the number of spectrophotometric reagents for copper in some different sample matrices.

Regression lines of calibration curves for the determination of nickel and copper ions are given in Table 4 for both ligands and metal ions and in buffered (citrate buffer, $pH = 5.0$) and unbuffered ($pH \cong 6.0$) solutions. Ni gives a linear calibration diagram for *PPP* and *QPP* from 0.5 to 10.0 μg/ml and from 0.2 to 5.0 μg/ml, respectively. The sensitivity can be estimated from the slopes of the calibration curves [17]. Limits of detection are calculated according to the IUPAC definition and recommendations [17] and are also given in Table 4. From the obtained results it can be seen that *QPP* is more sensitive than *PPP* and that higher sensitivity is obtained for Cu(II) than for Ni(II). In addition to the applicability of the method for the determination of relatively low concentration levels of nickel and copper, these reagents and the method might be used for the determination of metals in samples with higher metal ion concentration levels. The applicability of the method for the determination of nickel as a minor component in real samples of two bronzes has been demonstrated, and possible interferences have been studied. It was found that Be does not interfere, which might be an advantage for the determination of Ni in beryllium bronzes. Cations of Fe, Al, and Zr also do not interfere, while Mn, Co, and Cr do. Chlorides, sulfates, and nitrates as a possible anions present in dissolved bronze samples do not interfere. In Table 5, the determination of nickel

Table 4. Regression lines $A = a \cdot \gamma + b$ for the determination of Ni(II) and Cu(II) with *PPP* and *QPP*; limits of detection

Complex	a	b (ml/μg)	r^2	γ_L (μg/ml)
	$pH = 5.0$ (citrate buffer)			
Ni–*PPP*	0.013 ± 0.008	0.131 ± 0.003	0.9989	0.114
Ni–*QPP*	0.007 ± 0.007	0.335 ± 0.019	0.9978	0.045
Cu–*PPP*	0.003 ± 0.003	0.282 ± 0.008	0.9986	0.053
Cu–*QPP*	0.003 ± 0.004	0.374 ± 0.015	0.9975	0.040
	$pH \cong 6.0$ (unbuffered solutions)			
Ni–*PPP*	0.014 ± 0.008	0.152 ± 0.008	0.9986	0.099
Ni–*QPP*	0.020 ± 0.007	0.356 ± 0.011	0.9988	0.042
Cu–*PPP*	0.028 ± 0.018	0.422 ± 0.023	0.9970	0.036
Cu–*QPP*	0.068 ± 0.044	0.718 ± 0.023	0.9965	0.021

A: absorbance; γ: mass concentration (μg/ml); γ_L: limit of detection (μg/ml); a: y-axis intercept in absorbance units; b: slope (ml/μg); r^2: squared correlation coefficient

Table 5. UV/Vis spectrophotometric determination of nickel with *QPP* in real samples of bronzes compared with AA spectrometric determination (average of 5 independent determinations)

Bronze	UV/Vis w_{Ni}(%)	AAS
CuNi2Be.00	1.78 ± 0.02	1.85 ± 0.01
CuAl10Fe5Ni5	4.71 ± 0.03	4.82 ± 0.02

with *QPP* in real samples of two different bronzes is compared with AA spectroscopic determination; good agreement between the results is obtained.

The results obtained show that the proposed method is comparable in performance with AA spectroscopy. The advantage of this method can be extended to simultaneous determinations of several interfering ions if derivative spectroscopy is used [5, 6, 18–23]. Combined UV/Vis detection with flow injection analysis [24] and, especially, with separation methods like ion exchange [25], chromatogrpahic [26] and capillary zone electrophoresis [27], would of course be a method of choice when dealing with multicomponent samples with sub-ppm metal ion mass fraction levels.

Knowing the properties of the investigated nickel complexes with *PPP* and *QPP*, other applications of these complexes are under investigation. Due to the moleculare structure of these complexes, with perchlorate as an anion, a preliminary investigation was performed to check their use as a dye for wool fibres. Although commercial metal complex dyes are mainly anionic dyes, in some instances the cationic dyes can also be used successfully. The main characteristic of wool fibres is that they change their ionic character with the *pH* of the solution. At lower *pH*, wool has cationic character while at higher *pH* the anionic character is more pronounced, which is in good agreement with higher exhaustion of dyes obtained at higher *pH*. Further investigations on this application are in progress.

Experimental

A stock solution of nickel was prepared by dissolving of $Ni(NO_3)_2$ (Merck) in redistilled water. The solution was standardized volumetrically with *EDTA*. A stock solution of copper was prepared by dissolving the appropriate amount of $CuCl_2 \cdot 2H_2O$ (Merck) in redistilled water. The solution was standardized electrogravimetrically. For *pH* adjustment, standard buffer solutions (Titrival, Kemika) were used. All other chemicals and solvents were of reagent grade (Merck or Aldrich) and used without further purification.

The AA spectroscopic measurements have been performed using a Perkin Elmer AAS (Model 1100B). The IR spectra were recorded on a Perkin Elmer spectrophotometer (Model 257) using KBr pellets. The detailed structures of isolated solid *QPP* and Me–*QPP* complexes were determined by a Hitachi–Perkin Elmer mass spectrometer (Model RMU-60; 20 eV and 280 °C). For potentiometric titrations, a Potentiometer Metrohm E 436 was used. UV/Vis spectra have been recorded on a spectrophotometer Varian DMS-80 while the *pH* of the solutions has been measured with a microprocessor controlled Iskra *pH*-meter (Model MA 5740) using a combined glass/reference electrode.

Data evaluations for stability constants have been performed on an IBM compatible PC AT 386 computer.

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