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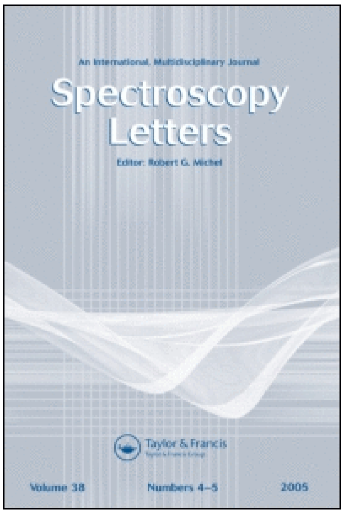

Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Koprivanac, N. , Meteš, A. and Papić, S.(1997) 'The Structures of the Chosen Metal Complexes with-2-[(2-Quinolylmethylene) amino]-phenol (QMAP) as a Ligand', Spectroscopy Letters, 30: 2, 181 — 192
To link to this Article: DOI: 10.1080/00387019708006980
URL: http://dx.doi.org/10.1080/00387019708006980

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SPECTROSCOPY LETTERS, 30(2), 181-192 (1997)

THE STRUCTURES OF THE CHOSEN METAL COMPLEXES WITH -2-[(2-QUINOLYLMETHYLENE)AMINO]-PHENOL (QMAP) AS A LIGAND

Keywords: 2-[(2-quinolylmethylene)amino]-phenol, complex structures, MS

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ABSTRACT

The new Mn(II), Cu(II) and Cr(III) complexes with 2-[(2quinolylmethylene)amino]-phenol (QMAP) were characterised by UV/VIS, IR and MS spectra and elemental analyses. The 1:1 (M:L) type of Mn(II)- and Cu(II)-QMAP complexes has been confirmed while the Cr(III)-QMAP complex show the ML_2 type of chelate molecule.

The structures and properties of the Mn(II), Cu(II), Cr(III), Ni(II) and Co(II) complexes with QMAP and PMAP (PMAP = 2-[(2-pyridylmethylene)amino]-phenol) were compared. The influence of the addition of another benzene ring to the ligand on the type of the formed complexes and on their solution or dyeing properties was investigated.

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INTRODUCTION

A very few papers published about the study of Shiff base 2-[(2-quinolylmethylene)amino]-phenol (QMAP) indicated that the structural and complex chemical investigations have not been fully explored.

M.Seyhan[1] synthesised and characterised QMAP only by the C, H analysis and melting point, while its UO_3 complex showed the 1:1 type of neutral molecule.

In a series of 35 Schiff base ligands, QMAP was also prepared and the catalitic behaviour (the decomposition velocity of H_2O_2 in the presence of the Cu(II), Co(II), Fe(II) and Mn(II) chelates) was surveyed[2].

The dipole moments, pk_a values, intramolecular H bond and IR spectrum of QMAP were studied by Russian scientists[3].

In a series of 40 ligands prepared, QMAP was only characterized by melting point and percentage of yield while the 1:1 Cu(I)-QMAP complex in isopenthyl and optimal pH range 5.5-5.6 were found[4]

The possibility of using QMAP as a spectrophotometric reagent for Co and Mn determination in solution[5] were given by group from our laboratory as well as the comparison of the structures, solution and dyeing properties of nickel complexes with QMAP and PMAP (PMAP = 2-[(2-pyridylmethylene)amino]-phenol)[6].

The new Mn(II), Cu(II) and Cr(III) complexes with QMAP are prepared and this paper is focused on a comparison of the structures of Mn(II), Cu(II), Cr(III), Ni(II) and Co(II) complexes with QMAP and PMAP and the influence of the addition of another benzene ring to the ligand on their properties.

EXPERIMENTAL

Measurements

Melting points, uncorrected, were determined on a Reichert thermovar HT1 B11 apparatus with a digital temperature indicator and a warmer Reichert Jung 620905.

Elemental analyses were performed in Institute "Ruđer Bošković", Zagreb, Croatia. IR spectra were run as Kbr pellets on a Perkin Elmer spectrometer (Model 257). The UV/VIS spectra were measured on a Pye Unicam spectrophotometer (Model SP-1800). The mass spectra were recorded on a Hitachi/Perkin Elmer model RMU-60 and a VG AutospecEQ mass spectrometer.

Materials

All chemicals and solvents were used without further purification.

Syntheses

The ligand QMAP was prepared from 2-quinolylcarbaldehyde and 1-amino-2-phenol according to the previously described procedure [1,4]. Recrystalizations from ether gave bright yellow crystals, m.p. 141,5-142,5 °C. Calc. for $C_{16}H_{12}N_2O$: C,77.40; H:4.88; N,11.28 %. Found: C, 77.40; H,4.89; N,11.30 %.

Manganese(II)-QMAP complex was prepared by addition of ligand (2,000 g) to a 50 mL of methanolic solution of $Mn(CH_3COO)_2$ $4H_2O$ (1.960 g) with stirring. Brownish red solution was stirred at room temperature for 2,5 hours and left to cool overnight. The brown crystals were filtered off and thoroughly rinsed with methanol (m.p. 271.8-273,9 °C). Calc.for $C_{16}H_{11}N_2OMnCH_3COO$: C,59.85; H,3.91; N,7.75 %. Found: C, 60.08; H, 4.19; N,7.59 %

Chromium(III)-QMAP complex was synthesised by addition of ligand (1.565 g) to a 50 mL of methanolic solution of $CrCl_36H_2O$ (1.676 g).The colour of the solution turns to dark red by stirring for 6 hours at room temperature. After cooling, dark red precipitation was filtered off and washed with MeOH (m.p. 338,2-340,0 °C). Calc. for $C_{32}H_{22}N_4O_2CrCl$: C, 66.04; H,3.81; N,9.63%. Found: C,66.21; H,3.88; N,9.79%.

Copper(II)-QMAP complex was prepared by addition of ligand (1.240 g) to a 60 mL of methanolic solution of $CuSO_4H_2O$ (1.000 g). The solution turned bluish red.

After stirring for 2 hours at room temperature, the green crystals with metallic lustre were washed with MeOH (m.p. 162.5-164.4 °C). Calc. for $C_{16}H_{11}N_2OCuCH_3COO$: C, 58.45; H,3.82; N,7.57%. Found: C,58.98; H,4.02; N,7.20%.

RESULTS

The UV/VIS spectra (data shown in Table 1) of all complexes show the bathocromic shifts of the absorption maxima due to formation of the metal-ligand complexes: 126, 150 and 156 nm for Mn(II), Cu(II) and Cr(III) complexes, respectively, related to the λ of A_{max} of QMAP.

The coordination of the metal ions with the donor atoms of the ligand produced the observed changes in the vibrational spectra of the Mn(II), Cu(II) and Cr(III) complexes. Their IR spectra obtained are summarised in Table 2 and only characteristic bands were discussed.

A sharp band in the spectrum of ligand at 3200 cm^{-1} due to free OH stretching of the phenol group is absent in the spectra of all complexes, confirming the bond formed between the oxygen of the phenol group and Mn(II), Cu(II) and Cr(III) ions.

The coordination of a nitrogen of the azomethine group with the metal ions is shown by shifts of the C-N stretching vibrations from 1620 $cm-^{1}$ to lower wavenumbers in the spectra of the complexes. The CN vibration in the conjugated cyclic system of the ligand appears at 1340 cm^{-1} and also shifts to lower wavenumbers in the spectra of the complexes, while the shifts of stretching frequencies ν(CO) are observed at higher wavenumbers, indicating the coordination of the metal ions with a nitrogen of the quinoline ring and with oxygen, respectively.

In the spectra of Cu(II) and Mn(II) complexes, two bands obtained about 1550 and 1420 cm^{-1} with deformation vibrations in the region 1020-930 cm^{-1} can be

TABLE 1: UV/VIS Data for QMAP and its Mn(II), Cu(II) and Cr(III) Complexes

COMPLEX	λ_{max} / nm in MeOH
QMAP	370, 295
Mn(II)-QMAP	496, 363, 302
Cu(II)-QMAP	520, 362, 300, 262
Cr(III)-QMAP	526, 374, 274

TABLE 2: Selected IR Bands for QMAP and its Cu(II), Mn(II) and Cr(III) Complexes

COMPOUND	$\tilde{v}$ (cm^{-1})							
	v(OH)	v(CN) azomet.	v(CC) arom.	v(COO) acetate	v(CN) kinol.	v(CO) phenol	δ(CC)	δ(CCO) acetate
QMAP	3200m	1620w	1585s 1500w 1480s 1430m	/	1340s	1210s	1170m 1040m 1000w	/
Mn(II)-QMAP	/	1580s	1550,1540,1505s,b 1475m 1460s	1410m	1310m	1250m	1170m 1130m 1120m 1100vs	1040w 1010m 950m 930m
Cu(II)-QMAP	/	1585s	1520s 1460m 1440m	1550s 1420m	1300s	1250s	1130m 1090m 830s	980w 940m
Cr(III)-QMAP	/	1580s	1550m 1510s 1470 1450m	/	1340,1320s	1260s	1180m 1140s 990s 950m	900,840w 740s

attributed to ν(C=O) and ν(C-O) vibrations of the acetate ion confirming the existence of the coordinated acetate group in the complex.

The changes in the vibrations produced by complexes formation allow conclusion to be drown concerning the occurrence of coordination in the chelate rings.

We already published the mass spectrum of QMAP but not its fragmentation, which is presented in Scheme 1.

Mass spectrum of the Cu(II)-QMAP complex (FIG. 1) confirms the ML stoichiometry and the existence of the acetate group in the coordination sphere.

The cleavage of the CH_3- and further of -C=O groups (of the acetate ion) from molecular ion (m/z 370) is confirmed by peaks at m/z 354 and 327 , respectively. The peak at m/z 311 correspnds to mass of copper atom coordinated to the ligand while the base peak at m/z 246 corresponds to the mass of deprotonated ligand. The difference of 93 mass units to the fragment at m/z 277 indicates the cleavage of the phenol group from the molecular ion.

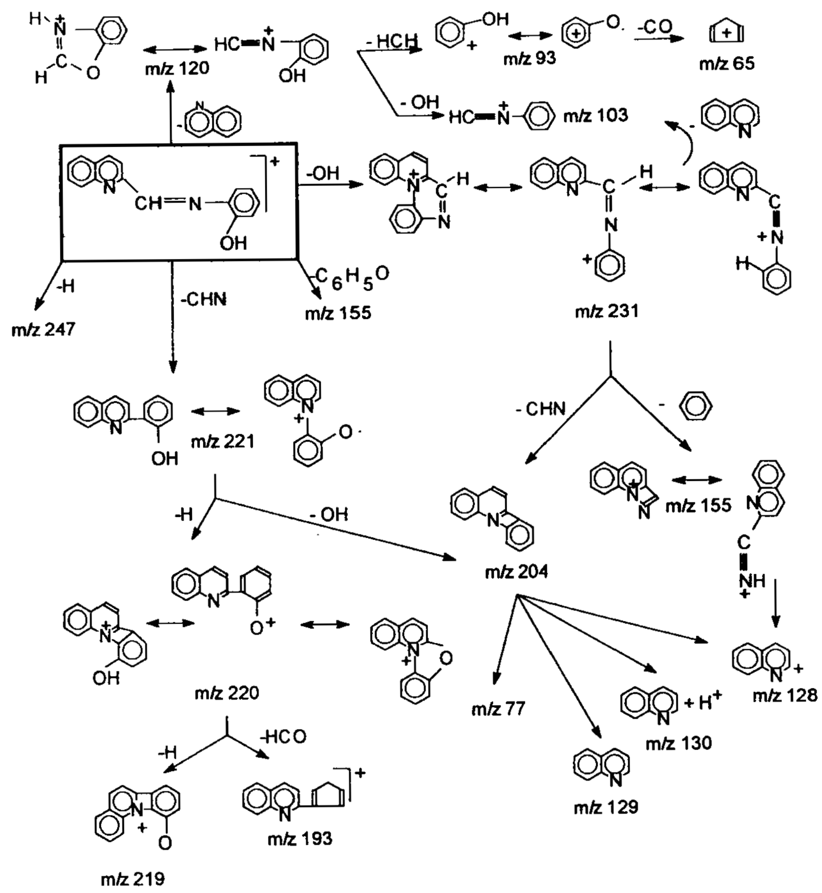
The same type of complex molecule confirms the mass spectrum of the Mn(II)- QMAP complex (FIG. 2). The molecular ion is observed at m/z 361 and the cleavage of the whole acetate group is observed by peak at m/z 302, confirming the 1:1 type of the complex. The cleavage of the $-CH_3$ and -C=O groups (of the acetate ion) and phenol group from molecular ion is also present, giving ions at m/z 346, 317 and 285, respectively. The base peak corresponds to the mass of the quinoline fragment ion.

For structure elucidation of the Cr(III)-QMAP complex, two ionization methods EI (FIG.3) and FAB (FIG.4) were performed. Apparently the complex is not sufficiently stable either under EI or FAB conditions to allow registration of a molecular ion.

The presence of two ligands is confirmed by peaks obtained by:

i) addition of the following mass units 93, 120, 128/130, 155, 193, 220, 231 to the ligand (m/z 247) giving the fragments at m/z 341, 367, 375, 402, 467, 478, respectively

ii) combination of two different parts of the ligand.



SCHEME 1: Fragmentation of QMAP

The significant peak m/z 299/301 indicates the coordination of chromium to the ligand. It further fragments: by the loss of oxygen (peak at m/z 284) and further of azomethine group (peak at m/z 257) or of phenol group (peak at m/z 205) or by loss of CHN first (peak at m/z 273) and then of OH (peak at m/z 257).

The addition of 35 mass units (m/z 334) and intensity of the peaks shows the presence of chlorine atom in the molecule, which is better seen in Fig. 4.

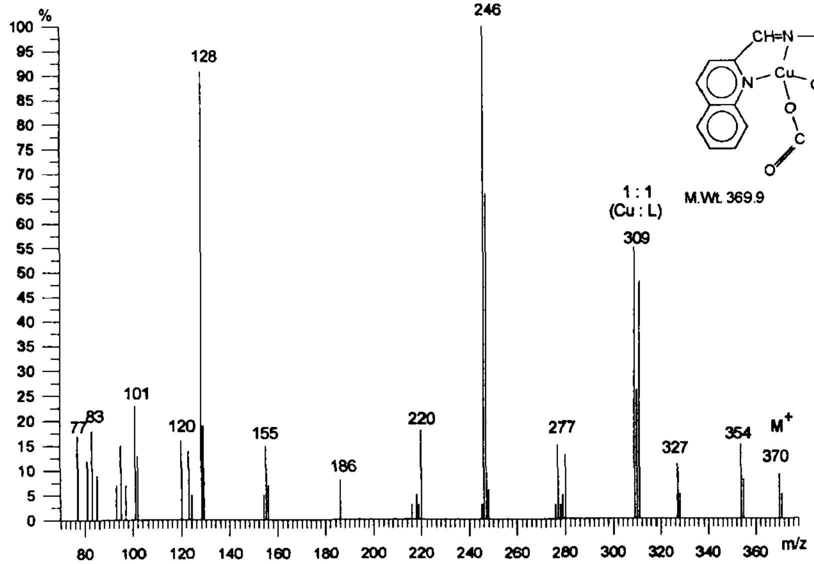


FIG. 1: Mass Spectrum of the Cu(II)-QMAP Complex

Chromium with chlorine atom together with ligand parts (m/z 93, 155, 220, 231 or 247) give the peaks at m/z 180, 242, 307, 318 and 334, respectively.

Therefore, the Cr(III)-QMAP complex show the 1:2, metal to ligand ratio, type of chelate structure with chlorine atom in the molecule.

DISCUSSION

Although the Mn(II)-PMAP[8] and Cu(II)-PMAP[10] complexes were isolated as perchlorates (because of better yields) and the Mn(II)-QMAP and Cu(II)-QMAP complexes as acetates, it is shown that Mn(II) ions form 1:1 type of the both complexes.

The X-ray diffraction data have shown that Cu(II) ions with PMAP form a very large cationic complex of M_2L_2 stoichiomety with an acetate as a bridging group between two copper ions and the perchlorate as anion[10], while with QMAP

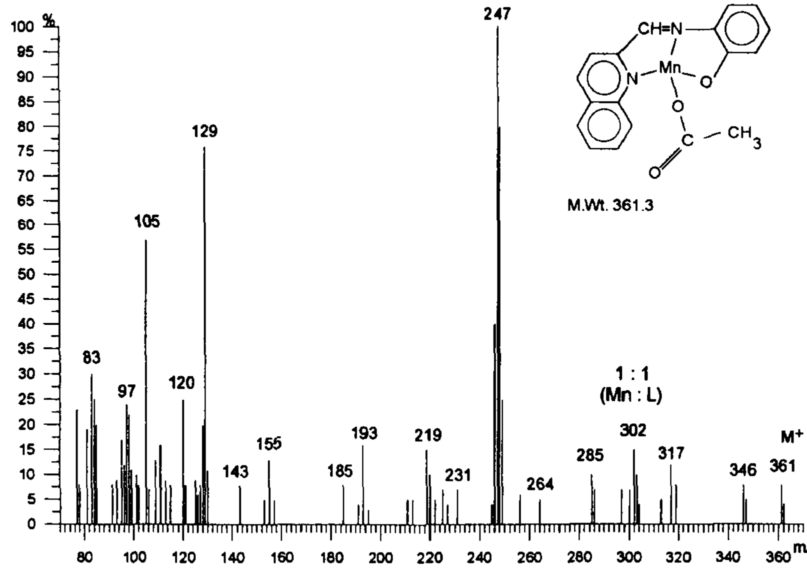


FIG.2: Mass Spectrum of the Mn(II)-QMAP Complex

form 1:1 type of chelate molecule with the acetate group in the coordination sphere.

Two PMAP ligands are coordinated to Cr(III) ion in the Cr-PMAP complex, forming the cationic complex with perchlorate as anion[7]. Two ligand molecules are also coordinated to cromium in the Cr(III)-QMAP complex, showing the ML_2 stoichiometry but with one clorine atom in the coordination sphere.

The Ni(II) ions with the PMAP and QMAP ligands also form different types of structures, the cationic 2:2 and neutral 1:2, respectively[6].

The Co(II) ions form cationic complexes with both ligands but with different metal-ligand ratio, 1:2 for the Co-PMAP[9] and 1:1 for Co-QMAP[5] complexes.

Comparing the values of molar absorption coefficients obtained for the metal complexes with PMAP and QMAP, which are always higher (bathochromic shifts of the absorption maxima), it can be concluded that chromophoric properties are

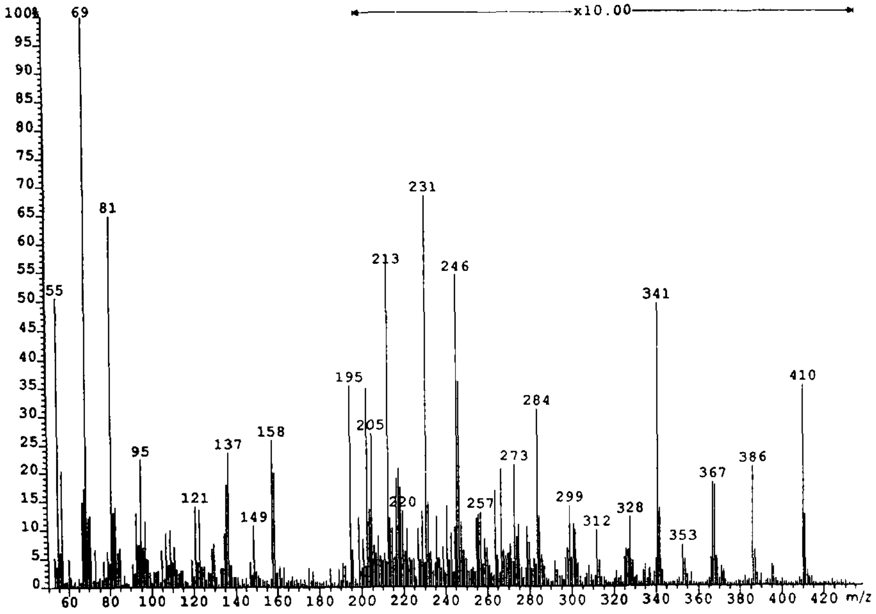


FIG.3: Mass Spectrum of the Cr(III)-QMAP Complex by the EI Ionization Method

enchanced by addition of the another phenyl ring to the ligand molecule. Furthermore, the research of their dyeing properties has shown that complexes with QMAP has also affinity for wool or sintetic fibres but generally the complexes with PMAP are much better dyes.

CONCLUSION

The metal to ligand ratio of all complexes is confirmed and the structural characterisation has relied on their MS spectra as well as the UV/VIS, IR spectra and elemental analysea.

The Mn(II) and Cu(II) ions with the QMAF ligand form neutral type of 1:1 (M:L) complexes with an acetate ion in the coordination sphere.

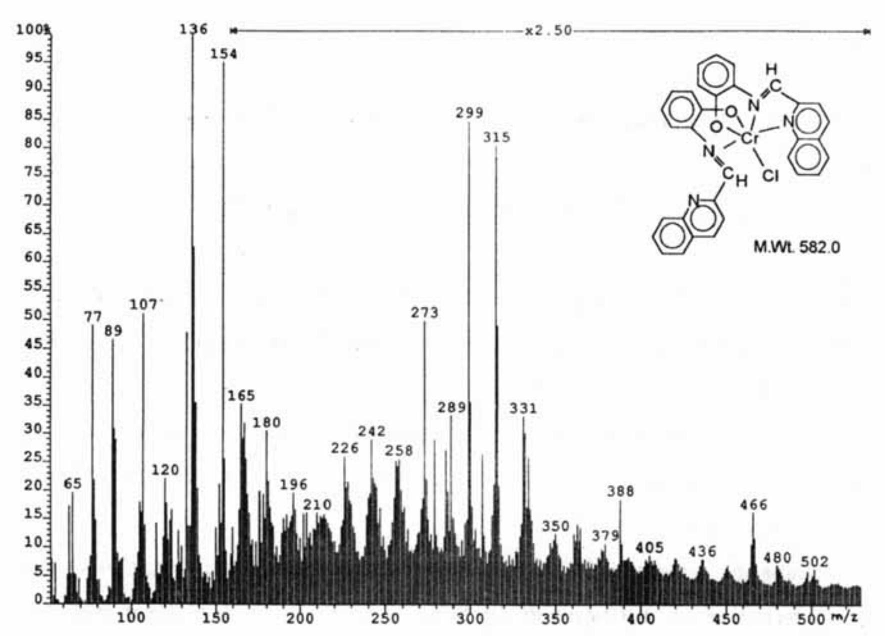


FIG.4: Mass Spectrum of the Cr(III)-QMAP Complex by the FAB Ionization Method

The QMAP compound behaves as a tridentate ligand and the coordination occures through the nitrogen of the quinoline and azomethine groups and through the oxygen of the hydroxy group. The coordination number of manganese and copper is 4.

The Cr(III)-QMAP complex form 1:2 (M:L) molecule where two oxygens and one chlorine saturate the primary valence of chromium, while two nitrogens from the azomethine groups and one from the quinoline group, with their spare elecrons, saturate its secondary valence. Therefore, because of the existence of chlorine, QMAP behaves as tridentate and bidentate ligand. The coordination number of chromium is 6.

We can conclude that the size of the ligand has not the significant influence on the type of chelate molecules but it has on their application properties.

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Received: June 24, 1996
Accepted: August 20, 1996