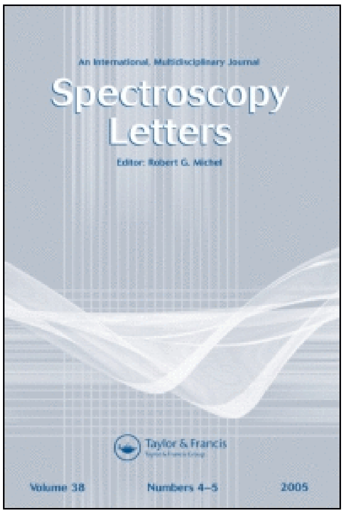

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The Solid Complexes of Ni(II), Co(II), Mn(II), and Cu(II) with 2-[(2-Pyrrolylmethylene) Amino]Phenol as a Ligand

N. Koprivanac[a]; A. Metes[a]; S. Papic[a]; B. Kralj[b]
[a] Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, CROATIA [b] Institute "Jozef Stefan", Ljubljana, Slovenia

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THE SOLID COMPLEXES OF Ni(II), Co(II), Mn(II),AND Cu(II) WITH 2-[(2-PYRROLYLMETHYLENE)AMINO]PHENOL AS A LIGAND

Keywords: 2-[(2-pyrrolylmethylene)amino]phenol, complexes, MS

N.Koprivanac, A.Meteš*, S.Papić and B.Kralj[#]
Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, CROATIA
[#]Institute "Jozef Stefan", Ljubljana, Slovenia

The complexes $Cu_2L_2\circ CH_3COO$, $Mn_2L_2\circ CH_3COO$, Ni_2L_2 and Co_2L_2, where L is 2-[(2-pyrrolylmethylene)amino]phenol (PYMAP), were synthesized and characterized by IR, UV/VIS and MS spectrometry and by elemental analysis. It has been found that PYMAP behaves as a tridentate dianion or as bidentate monoanion and tridentate dianion at the same time, which therefore forms various types of complexes. The Ni(II)- and Co(II)-PYMAP complexes form neutral chelates of M_2L_2 type, while the

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*Author for correspondence

Mn(II)- and Cu(II)-PYMAP complexes have the same M_2L_2 stoichiometry but with acetate in the inner coordination sphere.

INTRODUCTION

The PYMAP characterization[1] and behaviour as a bidentate monoanion as well as the nature and structure of the solid Zn, Cd and Ni complexes, with tetraedar ML_2 structure[2], were published by Spanish scientists. The Ni(II)-PYMAP system was also studied in solution where the 1:1 red complex was obtained[3].

Complexes of Zn(II), Pb(II), Pd(II) and Pt(II) were described with $ML(H_2O)$ structure and with the ligand as a tridentate dianion while of Cu(II), Fe(III) and Co(III) were obtained with the ligand as a bidentate monoanion. The obtained structures were $[Cu(LH)(OCH_3)H_2O]$ and $[M(LH)(X_2)\circ\circ(H_2O)_n]$ where M=Fe(III), Co(III) and X=acetylacetonate. The Schiff base behaviour either as a bidentate monoanionic ligand with pyrrole nitrogen intact and uninvolved in bonding to the metal, or as a tridentate dianion using the pyrrole deprotonated nitrogen was studied[4].

Thermodynamical and physicochemical investigation of several metal chelates with PYMAP were carried out[5].

Due to the different structures published for the same ligand and metals, previous works show that the ligand has various modes of coordination but that research has not been fully explored. Therefore, as part of an ongoing research, this work has been focussed on confirming the stoichiometry of the solid Ni(II), Co(II), Mn(II) and Cu(II) complexes with PYMAP and coordination between metal atoms and ligand donors.

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 "Ruder 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 VG AutospecQ mass spectrometer in Institute "Jozef Stefan", Ljubljana, Slovenia.

Materials

All chemicals and solvents were used without further purification.

Syntheses

The ligand was prepared by slight modification of an earlier methods[1,5,6]. Recrystallizations from ether gave thin light-yellow needles. M.p. 140.6-142.3°C (lit.[5,6] 134°C and 123-125°C). Calc. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04%. Found: C, 70.95; H, 5.44; N, 15.05%.

All complexes were prepared in a similar manner by stirring methanolic solution of the corresponding metal salts [Co(CH_3

$COO)_2 4H_2O$, $Ni(CH_3COO)_2 4H_2O$, $Mn(CH_3COO)4H_2O$ and $Cu(CH_3COO)_2H_2O$] and an equimolar amount of the ligand (0.01 mol), under reflux.

Ni(II)-PYMAP complex: the yellow crystals was isolated and recrystallized from MeOH (m.p. 292.7-294.0°C). Calc. for $C_{22}H_{16}N_4O_2Ni_2$: C, 54.39; H, 3.32; N, 11.53%. Found: C, 53.98; H, 3.40; N, 11.43%.

Co(II)-PYMAP complex, formed as brown precipitate, after recrystallization from MeOH was isolated as brown crystals with violet lustre (m.p. 300.1-302.3°C). Calc. for $C_{22}H_{16}N_4O_2 \cdot Co_2$: C, 54.34; H, 3.32; N, 11.52%. Found: C, 54.41; H, 3.66; N, 11.44%.

Mn(II)-PYMAP complex was isolated as yellow crystals which were then washed successively with MeOH (m.p. 333.7-336.0°C). Calc. for $C_{22}H_{17}N_4O_2Mn_2CH_3COO$: C, 53.55; H, 3.75; N, 10.41%. Found: C, 53.49; H, 4.10; N, 10.04%.

Cu(II)-PYMAP complex was obtained as dark green crystals which were then washed with MeOH (m.p. 275.1-275.5°C). Calc. for $C_{22}H_{17}N_4O_2Cu_2CH_3COO$: C, 51.89; H, 3.63; N, 10.09%. Found: C, 52.31; H, 3.87; N, 10.13%.

RESULTS AND DISCUSSION

Although the UV/VIS and IR spectra of obtained complexes gave an insight into the change of the structure as a consequence of the chelation, only mass spectrometry was successfully applied in a structure characterization and establishing the stoichiometry of the metal complex compounds.

The data of UV/VIS spectrs show the bathochromic shifts of the absorption maxima due to formation of the metal-ligand complexes: 130 nm, 193 nm, 147 nm and 145 nm for Ni, Co, Mn and Cu complexes *in chloroform, respectively, related to the* λ of A_{max} of PYMAP (λ=333 nm).

The mass spectra of Ni(II)- and Co(II)-PYMAP complexes (Fig.1 and 2) show the parent peaks at m/z 486, confirming the M_2L_2 type of neutral chelate molecules.

The spectrum of the Ni(II)-PYMAP complex (Fig.1) is dominated by two intense peaks, the parent peak and ion at m/z 243 (also the base peak) which corresponds to the mass of nickel atom coordinated to the ligand. The fragment at m/z 184 corresponds to the deprotonated ligand while the further fragmentation corresponds to the ligand itself.

In the spectrum of Co(II)-PYMAP complex (Fig.2), the base peak at m/z 184 corresponds to the mass of deprotonated ligand, while lower fragments are similar to those of the ligand itself. The peaks at m/z 427 and m/z 243 correspond to metal to ligand ratio 1:2 and 1:1, respectively. The cleavage of the azomethine group from the ligand and recombination of pyrrole and phenol fragments with the cobalt atom, results in the ion at m/z 216.

Those mass spectra confirm that PYMAP in Ni(II)- and Co(II)- -PYMAP complexes behaves as tridentate dianion. Also, it is evident that the metal atoms are coordinated through the nitrogen of two pyrrole groups and through the oxygen of two hydroxyl groups.

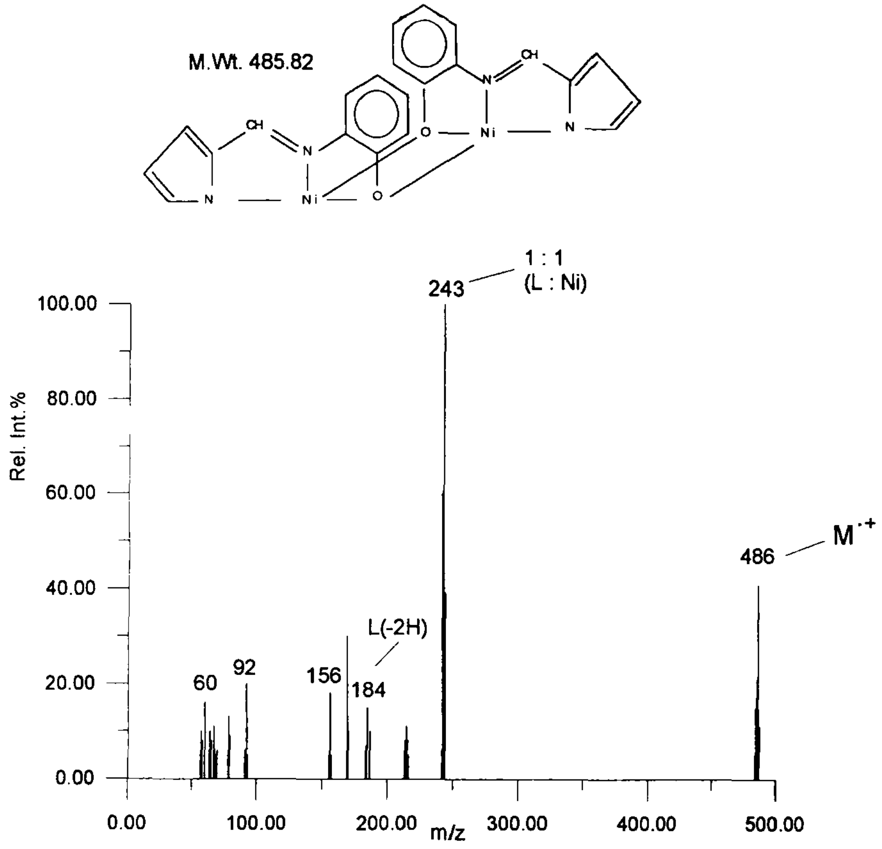

Fig. 1. Mass spectrum of the Ni(II)-PYMAP complex

In the mass spectra of Mn(II)-PYMAP complex (Fig.3), the fragment ions lower then the fragment at m/z 185, which corresponds to the mass of the ligand minus a hydrogen, are similar to those observed for the ligand itself. The exception is a peak at m/z 147 which corresponds to mass of a manganese atom attached to the phenol fragment or to the pyrrole and

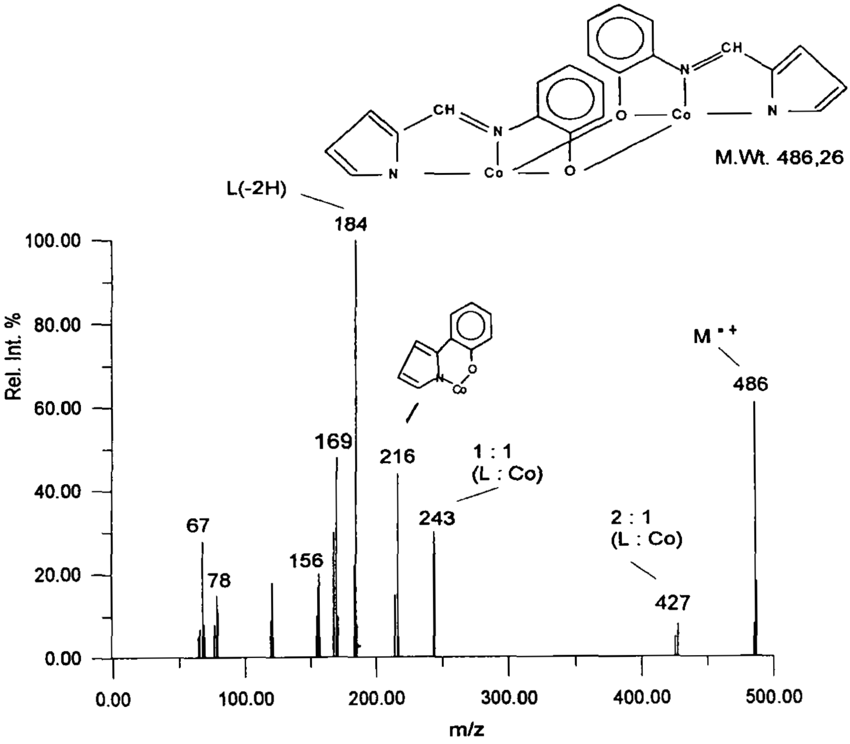

Fig.2. Mass spectrum of the Co(II)-PYMAP complex

azomethine fragments. The molecular ion, m/z 538, is observed at the calculated molecular mass. The base peak, m/z 238, corresponds to the metal to ligand ratio 1:1, while the peak at m/z 424 to 1:2.

The most important peaks are m/z 206 and m/z 353, as well as the parent peak, which confirm the existence of the acetate group in the coordination sphere. First one corresponds to the

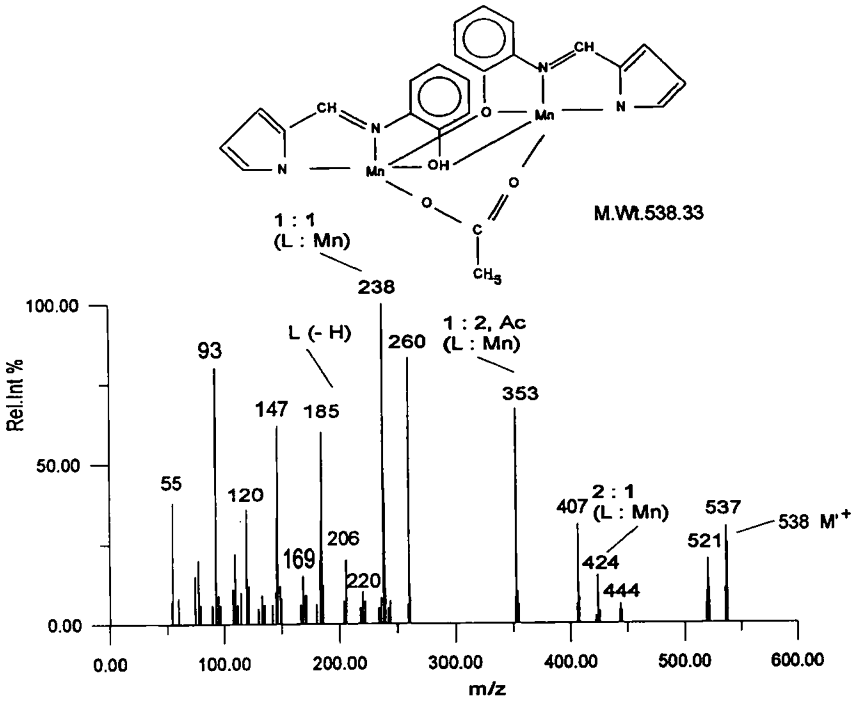

Fig.3. Mass spectrum of the Mn(II)-PYMAP complex

mass of the acetate group with the fragment m/z 147. The other one indicates the existence of two manganese atoms coordinated to the ligand through the acetate ion; the loss of the phenol group further results in obtaining the peak at m/z 260.

The cleavage of the hydroxyl group and the phenol group (m/z 93) results in obtaining the peaks at m/z 521 and m/z 444, respectively, but also indicates that oxygen of the OH group is once uninvolved in bonding to the manganese atom. At the same time, its coordination to the metal atom is evident by peaks m/z 184 (the mass of the ligand minus two hydrogens), m/z 239 (ML) and m/z 424 (ML_2).

The mass spectrum of the most abundant fragments for the Cu(II)-PYMAP complex is given in Fig.4. The base peak, m/z 247, corresponds to the copper attachement to the ligand (ML). The peaks at m/z 185 and m/z 184 correspond to the deprotonated ligand fragments, while the fragments with smaller mass confirm the fragmentatnion patern of the ligand itself. The molecular ion is observed at m/z 556. The fragment ion at m/z 496 corresponds to metal to ligand ratio 2:2 (M_2L_2).

The most important peaks are at m/z 370 and m/z 376. First one corresponds to the mass of one ligand and two copper ions conected through the acetate ion, while the other one corresponds to the same M_2L stoichiometry but with the another pyrrole fragment, indicating that both pyrrole nitrogens take place in the coordination to the copper ions.

The coordination of the metal iones to the ligand is further confirmed by the IR spectra summerized in Table 1.

The assignment of peaks for the Ni(II)-, Co(II)-, Mn(II)- and Cu(II)-PYMAP complexes was accomplished by comparison with the IR spectrum of PYMAP and only characteristic bands were discussed.

The disappearance of the sharp bands at 3440 and 3380 cm^{-1} observed in the IR spectrum of the PYMAP ligand itself, which correspond to the O-H (phenol) and N-H (pyrrole) vibrations of the ligand, can be seen in the IR spectra of Ni(II)- and Co(II)-PYMAP complexes.

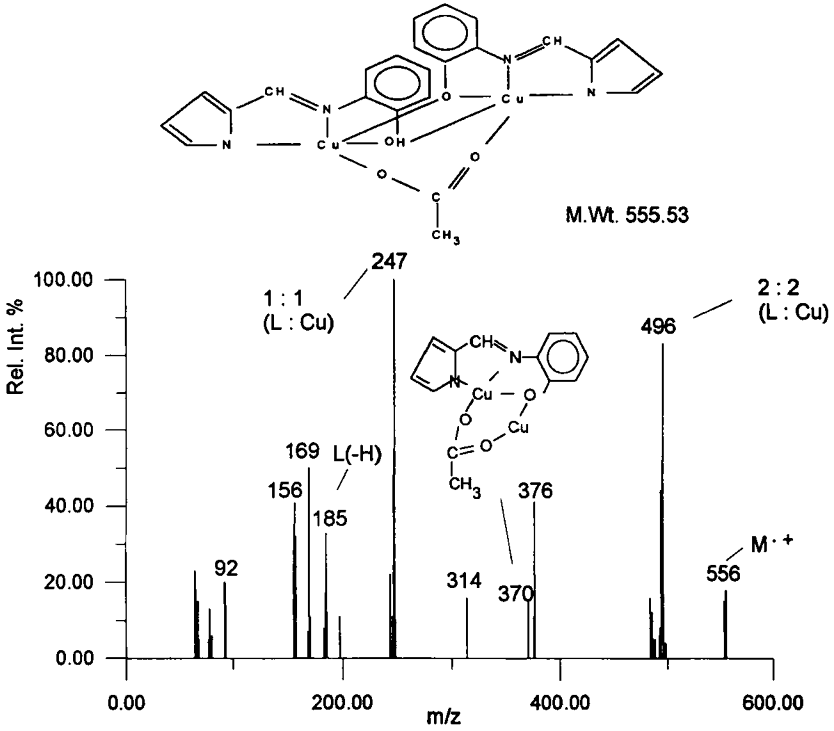

Fig.4. Mass spectrum of the Cu(II)-PYMAP complex

It confirms the coordination of the oxygen atom of the phenol group and the nitrogen atom of the pyrrole group to the nickel and cobalt ions.

This coordination is further confirmed by shift of the stretching frequencies ν(C-O) in phenol, from 1240 and 1210 cm^{-1} (PYMAP) to 1280 and 1250 cm^{-1} (Ni-PYMAP) and to 1275 and 1250 cm^{-1} (Co-PYMAP), and ν(C-N) in pyrrole, from 1330 cm^{-1} (PYMAP) to 1355 cm^{-1} (Ni-PYMAP) and to 1350 cm^{-1} (Co-PYMAP).

TABLE 1: Selected IR bands for PYMAP and its Ni(II), Co(II), Mn(II) and Cu(II) complexes

COMPOUND	$\tilde{\nu}$ (cm^{-1})							
	ν(OH)	ν(NH)	ν(CN) azomet	ν(CC) arom	ν(COO) acetate	ν(CN) pyr	ν(CO)	δ(COO) acetate
PYMAP	3440s	3380s	1620s	1590s 1580s 1480m 1450m 1410s	/	1330s	1240s 1210s	/
Ni-PYMAP	/	/	1615s	1580m 1540m 1475s 1410s	/	1355s	1280s 1250s	/
Co-PYMAP	/	/	1610s	1580m 1540w 1475s 1410s	/	1350s	1257s 1250s	/ /
Mn-PYMAP	3630m 3400v, b		1610s	1585s 1540s 1480s 1430s 1415s	1560s 1450m	1350m	1270s 1250s	1030s 955m 920m
Cu-PYMAP	3630m 3400v, b		1605s	1585m 1480s 1450m 1405s	1550m 1430m	1360-1355s	1280s 1260s	1035w 955m 920w

The band corresponding to the azomethine group in the ligand, found at 1620 cm^{-1} shifted to lower wavenumbers, 1615 cm^{-1} (Ni-PYMAP) and 1610 cm^{-1} (Co-PYMAP), and confirmed the coordination of the metal atoms to the azomethine group.

The strong bands at 3440 and 3380 cm^{-1} found for PYMAP cannot be seen in the IR spectra of the Mn(II)- and Cu(II)-

-PYMAP complexes, but a sharp band and 3630 cm^{-1} with very weak broad band about 3400 cm^{-1}, due to the ν(O-H) vibrations, are present. This indicates the coordination of the metal atoms with the pyrrole nitrogen as well as the existence of the free OH group.

Nevertheless, the shift of the C-O vibrations of phenol from 1240 and 1210 cm^{-1} to higher wavenumbers indicates the metal--oxygen linking.

The changes in the vibration produced by metal-ligand formation are also observed by the shift of the azomethine group to lower wavenumbers and of the C-N in pyrrole to the higher wavenumbers, indicating that hetero and azomethine nitrogens are involved in bonding to the manganese and copper ions.

The bands obtained at 1560 and 1450 cm^{-1} (Mn-PYMAP) or at 1550 and 1430 cm^{-1} (Cu-PYMAP), although the overlapping of C-C bands, can be attributed to carbonile vibrations of ν(C=O) and ν(C-O) from acetate. The frequencies and $\Delta\nu$ value of 120 cm^{-1}, with the deformation vibrations at 1030, 955 and 920 cm^{-1}, confirm the existence of the bridging acetate group in the complex molecules[7].

All data obtained for the Ni(II)- and Co(II)-PYMAP complexes suggest that PYMAP was coordinating to the nickel and cobalt ions through all donor atoms, behaving as tridentate bianion and forming M_2L_2 neutral chelate molecules.

For the Mn(II)- and Cu(II)-PYMAP complexes was found that two metal atoms, both coordinated to each ligand, were bridged by the oxygen from acetate forming stable binuclear complexes.

PYMAP was coordinating to manganese and copper through the two hetero and two azomethine nitrogens and to only one oxygen, behaving therefore as tridentate bianion and bidentate monoanion at the same time.

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