SDU Journal of Science (E-Journal), 2012, 7 (1): 1-8

Infrared and Micro-Raman Spectroscopic Studies of [M(1(2H)-phthalazinone)$_n$.Cl$_2$] (M = Co, Cu and Mn; n = 1, 2) Complexes

Nuri Öztürk[1], Semiha Bahçeli[1,]*

[1]*Department of Physics, Faculty of Arts and Science, Süleyman Demirel University, 32260, Isparta, Turkey*
**Corresponding author e-mail: semihabahceli@sdu.edu.tr*

Received: 25 April 2012, Accepted: 10 May 2012

Abstract: In this study, the Co(II), Cu(II) and Mn(II) metal halide complexes of 1(2H)-phthalazinone were characterized by elemental analysis, FT-IR and micro-Raman spectroscopies. The M(1(2H)-phthalazinone)$_n$.Cl$_2$ (M = Co, Cu and Mn; n = 1, 2) complexes have been prepared for the first time and their vibrational wavenumbers were reported. The results obtained experimentally indicate that the coordination between 1(2H)-phthalazinone and different metal ions gives different metal-oxygen stretching frequencies which decrease in the following order Co(II) > Mn(II) > Cu(II).

Key words: 1(2H)-phthalazinone, IR and Raman spectroscopies, Elemental analysis, Metal halide complexes.

[M(1(2H)-phthalazinone)$_n$.Cl$_2$] (M = Co, Cu and Mn; n = 1, 2) Bileşiklerinin Kırmızıaltı ve Mikroraman Spektroskopisi ile İncelenmeleri

Özet: Bu çalışmada, 1(2H)-fitalazinon Co(II), Cu(II) ve Mn(II) metal halid bileşikleri, elemental analiz, FT-IR ve mikro-Raman spektroskopileri ile karakterize edilmiştir. M(1(2H)-fitalazinon)$_n$.Cl$_2$ (M = Co, Cu ve Mn; n = 1, 2) bileşikleri ilk kez hazırlanmıştır ve titreşim dalgasayıları sunulmuştur. Deneysel olarak elde edilen sonuçlar, 1(2H)-fitalazinon ile metal iyonları arasındaki koordinasyonun, Co(II) > Mn(II) > Cu(II) olarak azalan metal-oksijen gerilme frekanslarını verdiğini göstermektedir.

Anahtar kelimeler: 1(2H)-fitalazinon, IR ve Raman spektroskopileri, Elementel analiz, Metal halid bileşikleri.

1. Introduction

Very recently, the analysis of molecular structure and vibrational spectra of the 1(2H)-phthalazinone molecule have been reported in both experimentally and theoretically using Hartree-Fock (HF) and Density Functional Theory (DFT/B3LYP) calculation methods [1]. This molecule which is an important membering heterocylic ring shows a wide range of pharmacological activities and is employed in medical chemistry [2-6]. Furthermore the 1(2H)-phthalazinone molecule,($C_8H_6N_2O$), belongs to monoclinic space group $P2_1/c$ and is almost planar with a dihedral angle of 0.52° between the two rings [7]. However the metal complexes of biologically important ligands can be more effective than free ligands [8, 9]. In this framework our interest in 1(2H)-phthalazinone is primarily due to its ligand properties with any metal cations. Up to our knowledge no study on the cobalt, copper and manganese metal halide complexes of the mentioned ligand have been reported.The purpose of this study is to present the results of IR and micro-Raman spectra and elemental analyses of metal halide complexes fromed 1(2H)-phthalazinone, with the divalent metal ions, Co(II), Cu(II) and Mn(II), for the first time.

2. Experimental details

2.1. Materials

The metal chloride salts ($CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $MnCl_2.2H_2O$) (99%) and 1(2H)-phtalazinone ($C_8H_6N_2O$) (99%) used in this study were obtained from commercial sources (Merck) and (Sigma-Aldrich), respectively and were used without any purification.

2.2. Preparation of samples

First, 1 mmol of 1(2H)-phthalazinone molecule and 1 mmol of each metal(II) chloride were separately dissolved in the 10 ml of ethanol. Then, the solution of the 1(2H)-phthalazinone was added to metal(II) chloride solution. The mixtures were stirred at room temperature for 24 h. The precipitations were filtered, washed with the ethanol and dried at room temperature.

2.3. IR and Micro-Raman Spectroscopy

IR spectra of the title complexes were recorded at room temperature on a Perkin Elmer Spectrum One FT–IR (Fourier Transformed Infrared) Spectrometer with a resolution of 4 cm^{-1} in the transmission mode. The prepared samples were compressed into self-supporting pellets and introduced into an IR cell equipped with KBr window.

On the other hand, the micro-Raman (μ-Ra) spectra of the mentioned complexes were recorded by using a Jasco NRS–3100 micro–Raman Spectrophotometer (600 lines/mm grating and high sensitivity cooled CCD) at room temperature in the region 50–3500 cm^{-1}. The spectrometer was calibrated with the silicon phonon mode at 520 cm^{-1} and microscope objective 100x was used. The 785 nm lines of the diode laser was used for excitation. The exposure time was taken as 10 s and 50 scans were accumulated.

2.4. Elemental Analysis

The prepared compounds, [M(1(2H-phthalazinone)$_n$.Cl_2] (M = Co, Cu and Mn; n = 1, 2), were analyzed by using a GmbH Vario CHNS model analyzer for C, H and N with the following results (found % / calculated %).

Co(1(2H)-phthalazinone)$_2$.Cl_2; C: 41.82/45.52, H: 3.44/2.87, N: 12.28/13.27
Cu(1(2H)-phthalazinone)$_2$.Cl_2; C: 44.82/45.03, H: 2.71/2.83, N: 13.15/13.13
Mn(1(2H)-phthalazinone).Cl_2; C: 36.13/35.33, H: 2.28/2.22, N: 10.60/10.30

3. Results and discussion

Micro-Raman and IR spectra of free and ligand 1(2H)-phthalazinone molecule to metal complexes are given in Fig. 1 (in the region 50-1800 cm^{-1}) and Fig. 2 (in the region 2600-3500 cm^{-1}) and Fig. 3 (in the region 400-4000 cm^{-1}), respectively. On the other hand the results obtained from the spectral data and the assignments of vibrational bands are summarized in Table 1 by taking into the consideration of a previously performed work for free 1(2H)-phthalazinone molecule [1].

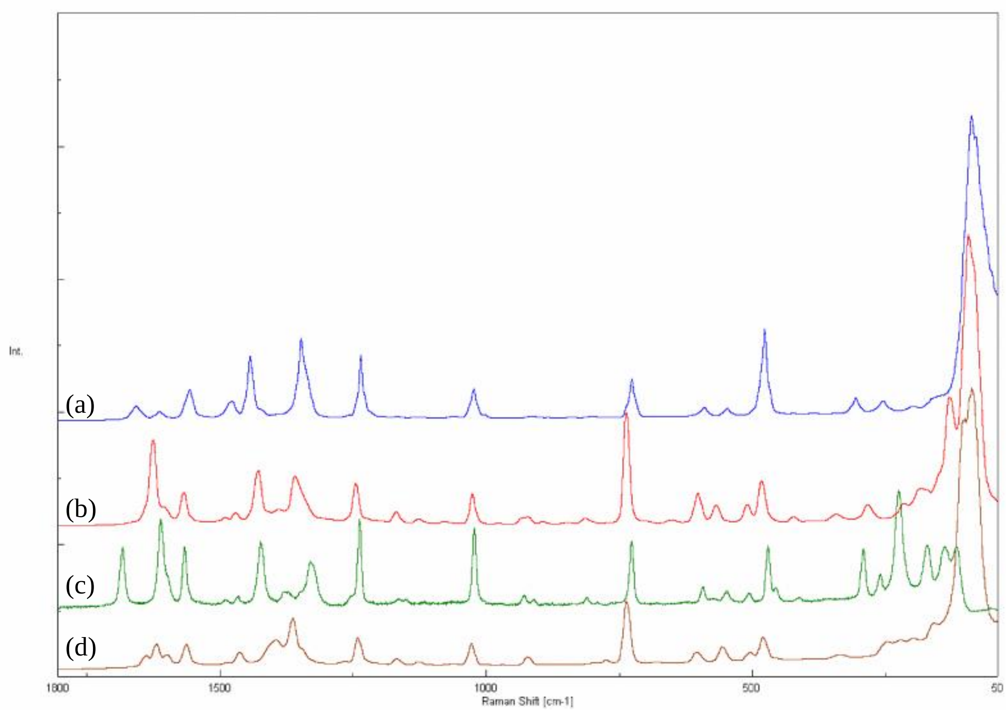

Figure 1. The µ-Raman spectra of (a) 1(2H)-phthalazinone molecule, (b) Co(1(2H)-phthalazinone)$_2$.Cl$_2$, (c) Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and (d) Mn(1(2H)-phthalazinone).Cl$_2$ complexes in 50-1800 cm^{-1} region.

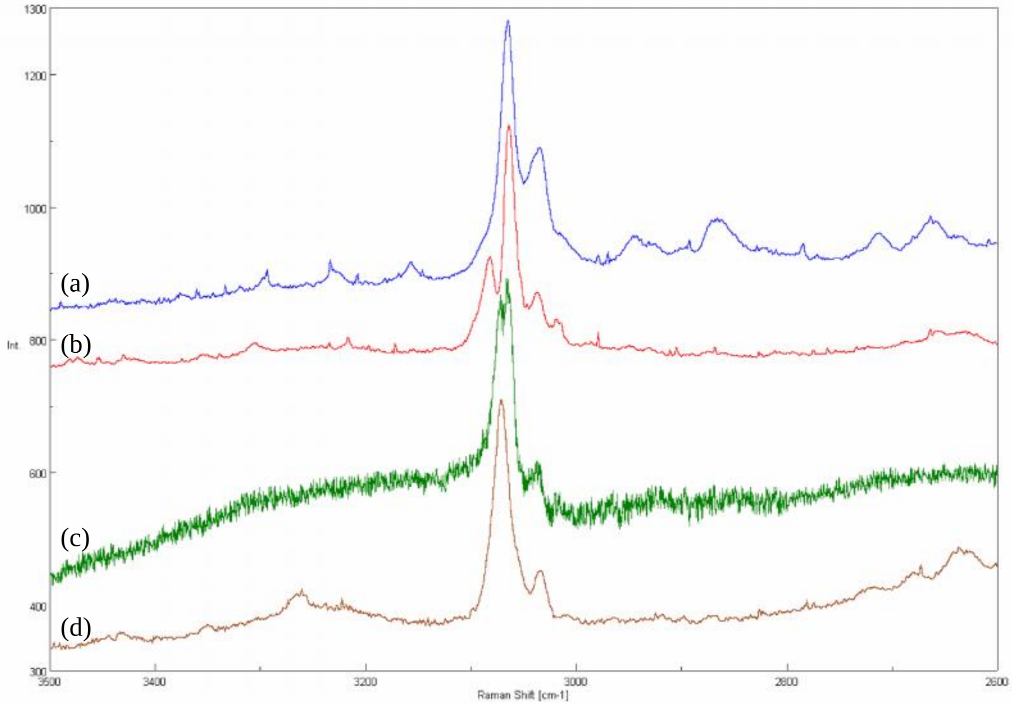

Figure 2. The µ-Raman spectra of (a) 1(2H)-phthalazinone molecule, (b) Co(1(2H)-phthalazinone)$_2$.Cl$_2$, (c) Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and (d) Mn(1(2H)-phthalazinone).Cl$_2$ complexes in 2600-3500 cm^{-1} region.

As seen in Table 1, 1(2H)-phthalazinone molecule gives three donor sites (a) two pyridine ring nitrogens and (b) carbonyl oxygen. As a monodentate ligand the bonding may take place through the pyridine ring nitrogens or the carbonyl oxygen. The frequency shifts on the vibrational bands of the metal complexes relative to those of free ligand molecule indicate clearly that the carbonyl oxygen of 1(2H)-phthalazinone is involved in the coordination in these complexes. It is known that if the coordination takes place through carboxyl oxygen it is expected that the C=O vibration shifts strongly [9].

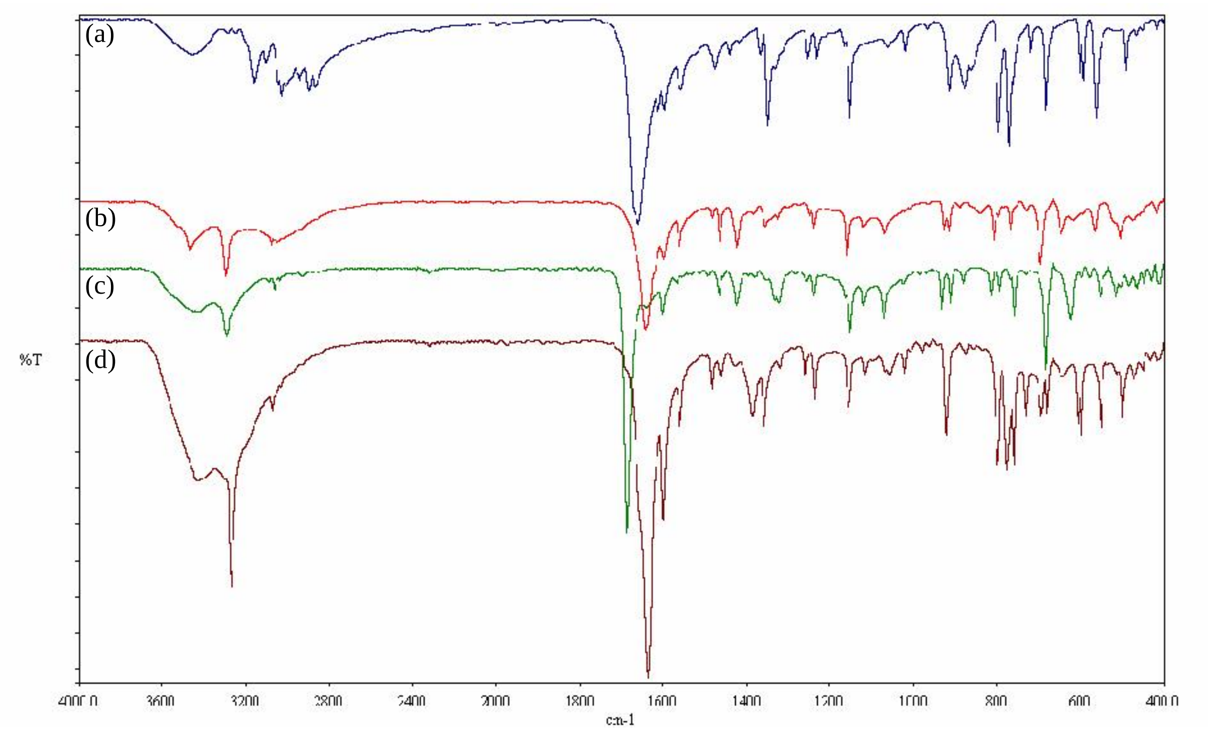

Figure 3. The FT-IR spectra of (a) 1(2H)-phthalazinone molecule, (b) Co(1(2H)-phthalazinone)$_2$.Cl$_2$, (c) Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and (d) Mn(1(2H)-phthalazinone).Cl$_2$ complexes.

As seen in Table 1, the N-H stretching band at 3291 cm^{-1} for IR and at 3297 cm^{-1} for μ-Raman spectra of 1(2H)-phthalazinone was observed at 3300 cm^{-1}, 3298 cm^{-1} and 3270 cm^{-1} in the IR spectra of metal complexes of 1(2H)-phthalazinone with Co, Cu and Mn, respectively and at 3304 cm^{-1} and at 3261 cm^{-1} in the μ-Raman spectra of complexes with Co and Mn, respectively, but not observed for the complex with Cu. As known the C-H stretching bands of aromatic compounds are usually observed in the range 3000-3100 cm^{-1} and separated from aliphatic C-H stretching bands which usually arise below 3000 cm^{-1} [10]. In high frequency region, the frequency shift on C-H stretching bands of metal complexes relative to free 1(2H)-phthalazinone indicate the coordination between 1(2H)-phthalazinone and metals. For instance, the C-H stretching band at 3104 cm^{-1} in IR spectrum of 1(2H)-phthalazinone was shifted to 3078 cm^{-1}, 3089 cm^{-1} and 3075 cm^{-1} in IR spectra of Co(1(2H)-phthalazinone)$_2$.Cl$_2$, Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes, respectively. Similarly, other frequency shifts on C-H stretching band in high frequency region can be seen in Table 1. On the other hand, overtone and combination bands were observed between 2889 cm^{-1} and 2868 cm^{-1} in the IR and μ-Raman spectra of pure ligand and its metal complexes.

Furthermore, in low frequency region, the observed bands at 1234 cm^{-1}, 1167 cm^{-1}, 1154 cm^{-1}, 1140 cm^{-1}, 1005 cm^{-1}, 968 cm^{-1}, 879 cm^{-1}, 862 cm^{-1}, 772 cm^{-1} and 762 cm^{-1} for IR spectrum of 1(2H)-phthalazinone and the bands at 1237 cm^{-1}, 1168 cm^{-1}, 1123 cm^{-1} and 1002 cm^{-1} for μ-Raman spectrum of 1(2H)-phthalazinone can be assigned to C-H bending modes.

Table 1. The vibrational wavenumbers and the assignments of 1(2H)-phthalazinone and metal complexes (cm^{-1}).

Pht.		$Co(pht)_2.Cl_2$		$Cu(pht)_2.Cl_2$		$Mn(pht).Cl_2$		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3291 w	3297 vw	3300 m	3304 vw	3298 m	-----	3270 w	3261 vw	N-H stretching
3104 m	3066 w	3078 w	3065 w	3089 w	3065 w	3075 m	3072 w	C-H stretching
3045 w	-----	3053 w	-----	3064 w	-----	3054 w	-----	C-H stretching
3030 m	3035 sh	3040 w	3038 vw	3036 w	3036 vw	3034 w	3034 vw	C-H stretching
1661 vs	1658 m	1643 vs	-----	1686 vs	1682 s	1638 vs	1639 w	C=O stretching
1612 m	1613 m	1619 sh	1624 s	1617 vw	1611 vs	-----	1619 m	C=N stretching
1597 m	-----	1599 m	1604 sh	1601 m	1600 sh	1601 s	1600 w	C=N stretching
1559 m	1556 m	1563 m	1568 m	1569 w	1566 s	1560 m	1562 m	C-C stretching
1479 m	1476 m	1484 m	1488 w	1493 m	1489 w	1485 m	1485 vw	C-C stretching
1440 m	1442 s	1466 m	1469 w	1468 m	1466 m	1460 w	1462 m	C-C stretching
1420 w	1423 sh	1424 m	1428 s	1425 m	1423 s	1430 w	-----	C-C stretching
1385 vw	1388 vw	1386 w	1390 w	1384 w	1374 m	1388 m	1393 w	C-N stretching
1367 m	1365 sh	1356 m	1359 s	1354 w	1363 w	1368 w	1363 s	N-H bending
1349 s	1347 s	1351 sh	-----	-----	1346 sh	1358 m	1345 sh	C-H bending
1332 w	1337 sh	1327 w	-----	1334 w	1328 s	1323 m	-----	C-C stretching
1254 m	1257 w	1250 w	------	1256 w	1251 sh	1260 m	1263 w	C-C stretching
1234 m	1237 s	1240 m	1245 s	1240 m	1238 vs	1238 m	1241 m	C-H bending
1167 w	1168 w	-----	1169 m	1164 w	1164 w	-----	1168 w	C-H bending
1154 s	-----	1160 m	-----	1153 m	-----	1158 m	-----	C-H bending
1140 sh	1123 w	1121 m	1126 w	1121 m	1114 w	1117 m	1127 w	C-H bending
1065 m	1061 w	1072 m	1078 w	1073 m	1065 w	1071 w	1060 w	N-N stretching
1021 m	1023 m	1022 m	1026 m	1025 m	1023 s	1022 m	1028 m	C-C stretching
1005 vw	1002 sh	1011 w	-----	1013 vw	-----	1008 w	1000 vw	C-H bending
968 m	-----	969 w	-----	974 w	-----	980 w	-----	C-H bending
915 m	912 w	916 m	923 m	912 m	929 m	908 sh	921 m	Ring bending
879 m	-----	889 m	-----	882 m	-----	877 m	-----	C-H bending
862 w	-----	868 sh	-----	865 vw	-----	858 w	-----	C-H bending
799 s	800 w	799 m	814 w	795 m	811 m	801 s	798 vw	Ring deformation
772 s	-----	768 w	-----	769 w	-----	777 m	-----	C-H bending
762 w	-----	-----	-----	759 m	-----	760 m	738 s	C-H bending
722 m	726 m	730 w	736 s	731 w	727 s	732 m	737 s	Ring stretching
683 s	-----	696 s	652 w	683 s	-----	680 m	-----	N-H bending
-----	-----	647 m	-----	625 s	-----	644 m	-----	M-O stretching
602 m	-----	618 m	-----	597 w	-----	606 m	606 w	N-H bending
593 m	590 m	595 w	604 m	578 w	593 m	598 m	605 m	N-H bending
563 s	547 m	567 m	567 m	554 m	545 m	553 s	557 m	N-H bending
492 m	490 sh	506 m	510 m	505 w	507 m	501 m	504 w	Ring deformation
468 w	478 s	478 w	483 s	484 m	472 s	474 m	480 m	Ring deformation

Table 2. (continued)

454 w	-----	460 w	-----	454 m		453 m	451 w	Ring deformation
432 w	423 w	429 w	424 w	429 m	413 w	433 m	423 vw	Ring deformation
418 w	-----	419 m	-----	418 w	-----	417 m	-----	Ring deformation
404 w	-----	406 w	-----	411 w	-----	411 sh	-----	Ring deformation
-----	-----	-----	343 m	-----	292 s	----	336 w	M-O stretching
-----	256 m	-----	282 m	-----	260 m	-----	245 w	Ring deformation
-----	-----	-----	216 w	-----	224 vs	-----	222 w	M–Cl stretching
-----	197 w	-----	185 m	-----	172 s	-----	198 w	Ring deformation
-----	152 m	-----	131 m	-----	139 m	-----	160 w	Ring deformation
-----	88 vs	-----	95 vs	-----	117 m	-----	89 vs	C-C-C bending

v; very, s; strong, m; medium, w; weak, sh; shoulder

On the other hand, C-C and C-N bands are observed in the same region and these bands are too difficult to distinguish. C-C and C-N single bond stretching bands of aromatic compounds are usually observed in the range 1300-1000 cm^{-1} and double bond stretching bands in the range 1650-1450 cm^{-1}. The C-C stretching bands of 1(2H)-phthalazinone were observed at the intervals 1597-1420 cm^{-1} and 1332-1021 cm^{-1} for IR spectrum and 1556-1423 cm^{-1} and 1337-1023 cm^{-1} for µ-Raman spectrum. The frequencies shifts in the IR and µ-Raman spectra of metal complexes in comparison with in 1(2H)-phthalazinone can be seen from Table 1.

The C=O strecthing bands of pyridine derivatives containing carboxyl group are usually expected to be higher than 1650 cm^{-1} [11]. A strong band at 1661 cm^{-1} in the IR spectrum and 1658 cm^{-1} in the µ-Raman spectrum of free 1(2H)-phthalazinone can be assigned to C=O stretching mode. This band was observed at 1643 cm^{-1}, 1686 cm^{-1} and 1638 cm^{-1} in the infrared spectra of Co(1(2H)-phthalazinone)$_2$.Cl$_2$, Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes, respectively. As seen in Table 1, this band was not observed in the µ-Raman spectrum of Co(1(2H)-phthalazinone)$_2$.Cl$_2$ but observed at 1682 cm^{-1} and 1639 cm^{-1} for µ-Raman spectra of Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes, respectively. These significant shifts in the spectra of metal complexes can be a result of coordination taken place through the carboxyl oxygen to the metal atoms.

The low-frequency vibrational modes and their assignments of all the complexes are also presented in Table 1. The new band at 647 cm^{-1}, 625 cm^{-1} and 644 cm^{-1} in IR spectra of Co(1(2H)-phthalazinone)$_2$.Cl$_2$, Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes, respectively, which was not observed for free 1(2H)-phthalazinone can be attributed the M-O stretching mode [12]. The metal–pyridine and metal halide vibrations are located in the region of 400–200 cm^{-1} [13]. Besides, the M–Ligand vibrations are observed in the higher region than the M–Cl vibrations. µ-Raman spectra of Co(1(2H)-phthalazinone)$_2$.Cl$_2$, Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes show a band at 343 cm^{-1}, 292 cm^{-1} and 336 cm^{-1}, respectively, and it can be assigned to M–O stretching mode [14]. We can clearly see that although the C=O stretching frequency value of Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ complex incrase relative to that of pure 1(2H)-phthalazinone when compared with the others, a contrary state occurs for the M-O stretching frequency value of the complexes. Similarly, the weak bands at 216 and 222 cm^{-1} for the cobalt and manganese complexes and the very strong band at 224 cm^{-1} for the cupper complex in their µ-Raman spectra were assigned M–Cl stretching mode [13].

4. Conclusions

M(1(2H)-phthalazinone)$_2$.Cl$_2$ (M= Co, Cu) and Mn(1(2H)-phthalazinone).Cl$_2$ complexes were synthesized for the first time. Vibrational assignments of infrared and µ-Raman spectra of pure ligand and its metal complexes were done by considering their experimental IR and µ-Raman spectra. The spectra of synthesized complexes and free ligand molecule were compared and the frequency shifts were indicated the formations of the complexes. From the spectral data, we also understood that the source of the coordination of metals is carbonyl oxygen of ligand. So, it is concluded that the carboxyl oxygen of 1(2H)-phthalazinone was involved in the formation of Co(1(2H)-phthalazinone)$_2$.Cl$_2$, Cu(1(2H)-phthalazinone)$_2$.Cl$_2$ and Mn(1(2H)-phthalazinone).Cl$_2$ complexes.

Acknowledgements

This work was supported by the Unit of the Management of Scientifical Research Projects within the Project No. 2102-D-10 of Süleyman Demirel University.

References

[1] Allan, J.R., Barnes, G.A.,Brown, D.H., 1971. Some transition metal complexes of pyridazine, pthalazine and 3,4-benzocinnoline, *Journal of Inorganic and Nuclear Chemistry*, 33 (11): 3765-3771.

[2] Riberio da Silva, M.A.V., Cabral, J.I.T.A., 2008. Experimental study on the thermochemistry of 1-(2*H*)-phthalazinone and phthalhydrazide, *The Journal of Chemical Thermodynamics*, 40 (5): 829–835.

[3] Doğruer, D. S., Küpeli, E., Yeşilada, E., Şahin, M. F., 2004. Synthesis of New 2-[1(2H)-Phthalazinon-2-yl]acetamide and 3-[1(2H)-Phthalazinon-2-yl]propanamide Derivatives as Antinociceptive and Anti-inflammatory Agents, *Archive der Pharmazie: Pharmaceutical & Medicinal Chemistry*, 337: 303−310.

[4] Cherkez, S., Herzig, J., Yellin, H., 1986. Synthesis, saludiuretic, and antihypertensive activity of 6,7-disubstituted 1(2H)- and 3,4-dihydro-1(2H)-phthalazinones, *Journal of Medicinal Chemistry*, 29 (6): 947-959.

[5] Kukovec, B.M., Kodrin, I., Mihalic, Z., Furic, K., Popovic, Z., 2010. *Cis–trans* isomerism in cobalt(II) complexes with 3-hydroxypicolinic acid. Structural, DFT and thermal studies, *Inorganica Chimica Acta*, 363 (8): 1887–1896.

[6] Ahuja, I.S., Prasad, I., 1976. Isonicotinamide complexes with some metal(II) halides and pseudohalides, *Inorganic and Nuclear Chemistry Letters*, 12 (10): 777-784.

[7] Büyükgüngör, O., Odabasoglu, M., Narayana, B., Vijesh, A.M., Yathirajan, H.S., 2007. Phthalazin-1(2*H*)-one, *Acta Crystallographica Section E: Structure Reports Online*, E63 (7): o3198.

[8] Gökce, H., Bahçeli, S., 2010. Analysis of molecular structure and vibrational spectra of 1(2H)-phthalazinone, *Journal of Molecular Structure*, 967 (1-3): 42–46.

[9] Nakamoto, K., 2009. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry, *6th ed., John Wiley & Sons, Inc., New York*, p. 424.
[10] Stuart, B.H., 2004. Infrared Spectroscopy: Fundamentals and Applications, *John Wiley & Sons, England*, p. 242.
[11] Silverstein, R.M., Webster, F.X., 1998. Spectroscopic Identification of Organic Compound, *6th ed., John Wiley & Sons, New York*, p. 512.
[12] Lane, T.J., Nakagawa, I., Walter, J.L., Kandathil, A.J., 1962. Infrared Investigation of Certain Imidazole Derivatives and their Metal Chelates, *Inorganic Chemistry*, 1 (2): 267-276.
[13] Bardak, F., Ataç, A., Kurt, M., 2009. Infrared and Raman study of some isonicotinic acid metal(II) halide and tetracyanonickelate complexes *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 71 (5): 1896–1900.
[14] Berney, C.V., Weber, J.H., 1967. Complexes of sulfoxides. II. Metal-oxygen stretching vibrations in complexes of dimethyl sulfoxide and dimethyl sulfoxide-d6 and the point group of the cation, *Inorganic Chemistry*, 7 (2): 283-287.

Nuri Öztürk e-mail: nuriozturk@sdu.edu.tr