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Spectroscopic and magnetic properties of Cu(II) complexes with selected biologically important ligands

Research Article

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Abstract: The aim of this work was to study the spectroscopic and magnetic properties of copper(II) *o*-, *m*-, *p*-aminobenzoates, *o*-, *m*-, *p*-methoxybenzoates and *o*-, *m*- and *p*-nitrobenzoates. The complexes were synthesized and their compositions were evaluated by elementary analysis. The infrared and Raman spectra for Cu(II) aminobenzoates, methoxybenzoates and nitrobenzoates were recorded and assigned. The obtained data were compared with those previously published for aminobenzoic, methoxybenzoic and nitrobenzoic acids and their sodium salts. The structures of Cu(II) *o*-, *m*-, *p*-aminobenzoates, *o*-, *m*-, *p*-methoxybenzoates and *o*-, *m*- and *p*-nitrobenzoates as well as the change in the electronic charges distribution caused by Cu(II) complex formation were discussed.

Keywords: *Methoxybenzoate • Aminobenzoate • Nitrobenzoate • Spectroscopic study • Magnetic study*

1. Introduction

Methoxybenzoic acids (*o*-, *m*- and *p*- anisic acids, MBA) are derivatives of benzoic acid that possess antibacterial properties and characteristic odours. *p*-Anisic acid is a constituent of anise oil (*Oleum Anisi*) – a colourless and light yellow liquid with a characteristic anetol smell and sweet taste. Anise oil possesses antiseptic, aperient, and vermifuge properties and is very effective in clearing congestion in the lungs and the respiratory tracts in conditions like asthma or bronchitis [1]. *p*-Anisic acid is a constituent of water extract from *Tabebuia impetiginosa* that has strong antifungal and anti-yeast properties against *Candida, Aspergillus, Staphylococcus, Streptococcus, Helicobacter pyroli, Brucella* [2,3]. Nitrobenzoic acids (NBA) are often chosen as sensitizing ligands to study the fluorescence enhancement of lanthanides. The aminobenzoic acids (ABA) are biologically active aromatic amino acids. Their antimutagenic properties depend on the position of substituent in the ring and decrease along the series: o-ABA>m-ABA>p-ABA [4]. The molecular structure of these compounds is a very important factor that influences their absorption and metabolism in the organism. Moreover, o-aminobenzoic acid is Vitamin L, and p-aminobenzoic acid is known as Vitamin B and bacterial Vitamin H. Richards and Xing studied the antibacterial properties of p-aminobenzoic acid and its effect on bacterial DNA synthesis [5]. Still growing interest in scientific research concerning the effect of metal ions on the electronic systems of carboxylic ligands is based on the great biological importance of metal-ligand interactions. Carboxylic complexes with copper(II) ion are of great importance due to their antimicrobial properties. The antimicrobial uses of copper include production of fungicides, pesticides, antifouling paints, antimicrobial medicines, oral hygiene products, hygienic medical devices, antiseptics and a host of other useful applications. Copper compounds are effective against

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Escherichia coli, *Legionella pneumophila*, *Actinomuicor elegans*, *Bacterium linens*, *Tuorolopsis utilis, Acromobacter fischeri, Photobacterium, Phosphoreum, Mercenaria mercenaria, Polio virus, Paramecium caudatum, Compylobacter jejuni,* and *Salmonella entrica*. The newest research points to copper as one of the most effective agents against *Clostridium difficile* - one of the most resistant hospital bacteria.

In this paper copper(II) *o*-, *m*- and *p*-aminobenzoates (AB), *o*-, *m*- and *p*-methoxybenzoates (MB) as well as *o*-, *m*- and *p*-nitrobenzoates (NB) were synthesized. On the basis of spectroscopic and magnetic data, the molecular structure of these compounds was studied, including the type of metal coordination.There is a general dependency between the difference in the value of the IR wavenumbers of the asymmetric ν_{as}(COO-) and the symmetric ν_s(COO-) stretches of the carboxylate group and the types of COO- group coordination [6]: (a) for bidentate chelating structure the bands of ν_{as}(COO-) and ν_s(COO-) in the IR spectra of studied complex are shifted to lower and higher wavenumbers, respectively, compared to appropriate ones for sodium salt; in other words: $\Delta\nu$(COO-) complex << $\Delta\nu$(COO-) sodium salt; (b) in case of bidentate bridging geometry both ν_{as}(COO-) and ν_s(COO-) bands in the IR spectra of studied complex are moved to higher wavenumbers compared to the location of these bands in IR spectra of sodium salt; $\Delta\nu$(COO-) complex ≤ $\Delta\nu$(COO-) sodium salt; (c) for monodentate type of coordination the bands of ν_{as}(COO-) and ν_s(COO-) in the IR spectra of the studied complex are shifted to higher and lower wavenumbers, respectively, compared to the corresponding ones in IR spectra of sodium salt; $\Delta\nu$(COO-) complex >> $\Delta\nu$(COO-) sodium salt.

Ishioka and co-workers studied correlations between wavenumbers of the $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ vibrations from the IR spectrum of zinc acetate and the type of carboxylate group coordination. They suggested that additional parameters should be taken into account, namely the band wavenumbers assigned to deforming in-plane vibrations of carboxylate group: $\beta_{as}(COO^-)$ and $\beta_s(COO^-)$ [7]. This proposition resulted from very little difference between the location of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands in the IR spectra of hydrated and anhydrous zinc acetate, which caused a small value of the parameter, $\Delta\nu(COO^-)$, *i.e.*, 113 cm^{-1} for hydrated and 118 cm^{-1} for anhydrous compounds. Whereas the difference in the location of $\beta(COO^-)$ bands is considerable (50 cm^{-1}) and, according to the authors, it is a crucial factor that enables distinguishing of the two different types of metal coordination present in anhydrous and hydrated zinc acetate, *i.e.*, bidentate bridging and bidentate chelating, respectively.

2. Experimental procedure

Copper(II) complexes were obtained by adding $CuCl_2$ solution (C= 0.2 mol dm^{-3}) to solutions of sodium aminobenzoates and methoxybenzoates (C= 0.2 mol dm^{-3}) in a stoichiometric ratio of 1:2. Colored precipitates were washed with distilled water. The composition of obtained compounds was determined by use of elemental analysis and is as follows: *o*-AB $Cu(C_7H_6O_2N)_2$; *m*-AB $Cu(C_7H_6O_2N)_2 \bullet H_2O$; *p*-AB $Cu(C_7H_6O_2N)_2 \bullet 2H_2O$; *o*-, *m*- i *p*-MB $Cu(C_8H_7O_3)_2$; *o*-NB $Cu(C_7H_4O_2NO_2)_2 \bullet ½H_2O$; *m*-NB $Cu(C_7H_4O_2NO_2)_2 \bullet ½H_2O$; *p*-NB $Cu(C_7H_4O_2NO_2)_2 \bullet H_2O$.

IR spectra were recorded with an Equinox 55 spectrometer (Bruker) within the range of 400-4000 cm^{-1}. Samples in the solid state were measured in KBr matrix pellets obtained with hydraulic press under 739 MPa pressure. Moreover, FT-IR spectra of the studied compounds were registered by the use of ATR accessory. Raman spectra of solid samples in capillary tubes were recorded in the range of 100-4000 cm^{-1} with a FT-Raman accessory of a Perkin - Elmer system 2000. The resolution of the spectrometer was 1 cm^{-1}.

Magnetic susceptibilities of polycrystalline samples of *o*-, *m*- and *p*-AB of Cu(II); *o*-, *m*- and *p*-MB of Cu(II); and *o*-, *m*- and *p*-NB of Cu(II) were measured in the temperature range of 76-303 K by the Gouy method using a sensitive Cahn RM-2 balance. The samples were placed in a long cylindrical tube which was suspended from an analytical balance. The sample tube was positioned between the poles of the magnet such that one its ends was in the region of homogeneous field and the other end was in the region of zero field. The force exerted on the sample was a function of the volume occupied by the sample in the field gradient. This force may be written in scalar form as a function of the isotropic volume susceptibility. Measurements were carried out at a magnetic field strength of 9.9 kOe. The calibrant employed was $Hg[Co(SCN)_4]$, for which the magnetic susceptibility was assumed to be 1.644×10^{-5}cm^3 g^{-1}. Corrections for diamagnetism of the calibrant atoms were calculated by the use of Pascal's constants [8,9]. Magnetic moments were calculated from Eq. 1:

$$\mu_{eff} = 2,83\ (\chi_M \cdot T)^{1/2} \qquad (1)$$

In the current paper, not all questions connected with the structure of copper(II) complexes were answered. In the further analysis of the electronic charge distribution in the studied molecules, the following methods will be applied: EPR spectroscopy, electronic absorption spectroscopy UV/VIS, and quantum-mechanical calculations. In case of problems with monocrystal synthesis, powder diffraction will be used.

3. Results and discussion

3.1. Spectroscopic studies

Band wavenumbers from FT-IR and FT-Raman spectra of amino-, methoxy- and nitrobenzoic acids as well as copper(II) and sodium amino-, methoxy- and nitrobenzoates were gathered in Table 1. The exemplary FT-IR and FT-Raman spectra of *o*-aminobenzoic acid are shown on Fig. 1. The assignments were done on the basis of literature [10,11] and published – yet quantum-mechanical – calculations performed in the Gaussian program [12]. The applied nomenclature corresponds to the numbering used by Varsányi [13].

In the spectra of aminobenzoic acids and copper(II) and sodium aminobenzoates, bands assigned to stretching vibrations of $-NH_2$ were present in the range 3500-3100 cm^{-1}. In the spectra of sodium and copper compounds, these bands were considerably shifted to lower wavenumbers compared with the corresponding bands from spectra of acids. Movement of the $\nu(NH_2)$ band toward lower wavenumbers indicates participation of the amino group in metal complexation. Changes in the location of the $\nu(NH_2)$ bands were significantly bigger (about 100-200 cm^{-1}) in the spectra of copper complexes than in those of sodium salts. This is caused by higher stability of copper(II) aminobenzoate complexes than sodium aminobenzoates. Bands derived from deforming vibrations of the amino group, $\beta(NH_2)$ and $\gamma(NH_2)$, were present in a similar range of wavenumbers. The location of bands assigned to stretching vibrations of the carboxylate group depends on the type of metal coordination [6]. On the basis of spectroscopic criteria, the type of copper(II) coordination may be discussed. In case of sodium *o*-AB, the value of $\Delta\nu(COO^-)$ amounted to 140 cm^{-1}, whereas for copper(II) *o*-AB, $\Delta\nu(COO^-)$ = 175 cm^{-1}. Additionally, in the IR spectra of this compound, the $\nu_{as}(COO^-)$ band was shifted toward higher wavenumbers and $\nu_s(COO^-)$ toward lower wavenumbers compared with the locations of the corresponding bands in the IR spectra of sodium *o*-AB. This indicates that in the *o*-aminobenzoate molecule, the copper ion is coordinated by a monodentate carboxylate group. Similar changes in the location of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands were observed in the IR spectra of copper(II) *m*-AB. The value of $\Delta\nu(COO^-)$ amounted to 170 cm^{-1} for copper(II) *m*-AB, whereas for sodium *m*-AB it was $\Delta\nu(COO^-)$=148 cm^{-1}. This suggests a monodentate carboxylate group in copper(II) *m*-AB, as well. In the case of copper(II) *p*-AB, $\Delta\nu(COO^-)$ amounted

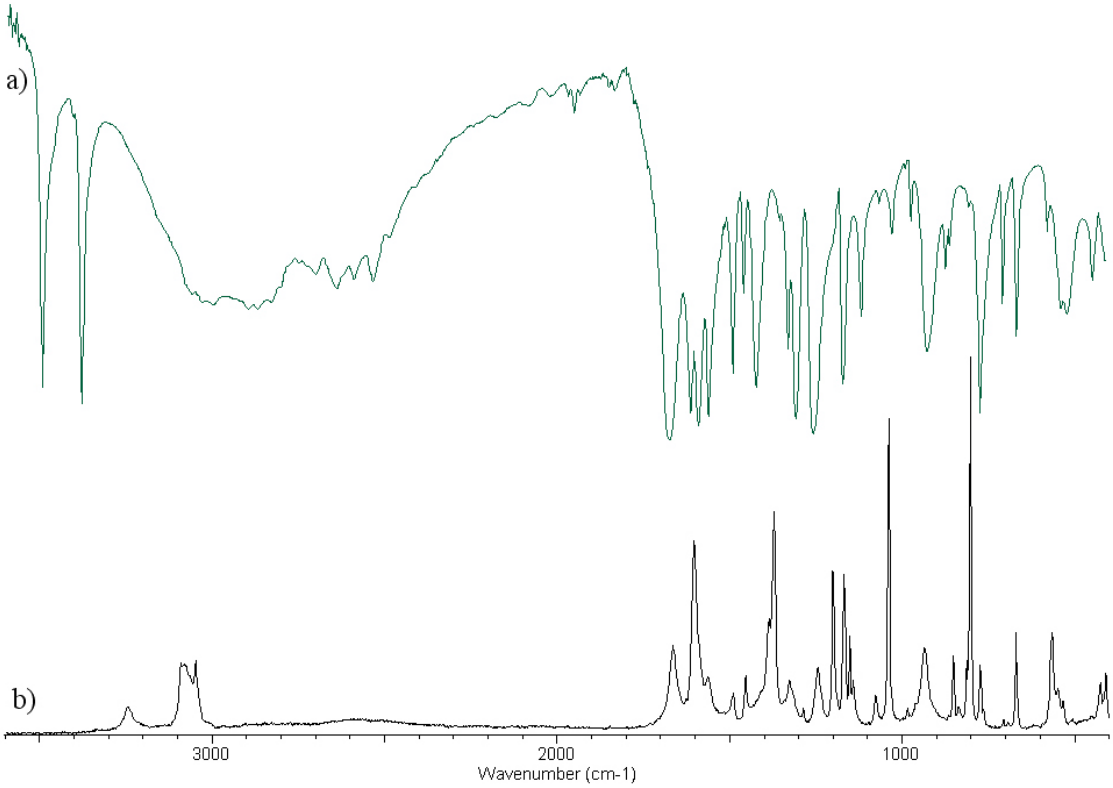

Figure 1. The FT-IR (a) and FT-Raman (b) spectra of *o*-aminobenzoic acid.

Table 1. Wavenumbers [cm^{-1}] of selected bands from the FT-IR and FT-Raman spectra of *o*-, *m*- and *p*-AM, MB and NB acids as well as their complexes with copper(II) and sodium ions.

		$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\beta_s(COO^-)$	$\beta_{as}(COO^-)$	19a	19b	18b	16b	13	10a	8a	8b	7a	7b	6a	5	4
								***o*-aminobenzoic [22]**												
Acid	IR	3495	3382					1455	1487	1061	438	1166		1586	1610			531	967	702
	Raman		3241					1453	1488	1076	425	1167		1583	1603			534	961	706
Na	IR	3428	3330	1531	1391	839	582	1449	1485	1065	426	1151		1581	1611			526	956	709
	Raman		3330	1538	1405	842	580	1452	1487	1069		1153		1576	1610			531		
Cu	IR	3276	3123	1552	1377	810	588	1459	1492	1084	424	1152		1583	1607			519	953	716
	IR_{ATR}	3273	3123	1555	1379	814		1460	1493			1152			1601				947	706
								***m*-aminobenzoic [22]**												
Acid	IR	3427	3335		1388			1450	1484	1095		1220	821	1563			918	507		675
	Raman				1383			1449	1483	1093		1225	828	1582			912	502		667
Na	IR	3427	3335	1561	1413	881	621	1454	1488			1222		1518	1594		927	514		677
	Raman			1565	1424			1462						1607	1592					675
Cu	IR	3241	3136	1575	1405	871	593	1458	1492	1107		1240	802	1617			927	529		679
	IR_{ATR}	3235	3134	1570	1400	881	588	1458		1099		1244					924			679
								***p*-aminobenzoic [22]**												
Acid	IR	3461	3364					1530	1446		501		822	1601	1573	1130				700
	Raman							1511	1434		504		828	1602		1132				700
Na	IR	3388	3205	1541	1407	622	534	1491			501		824	1601		1130				693
	Raman				1435			1521			537			1618						697
Cu	IR	3419	3132	1534	1389	633	521	1506	1436				803	1609		1145				701
	IR_{ATR}	3395	3138	1512	1393	630							812	1609		1130				696
		$\nu_{as}(CH_3)$	**$\nu_{as}(CH_3)$**	**$\nu_{as}(COO)$**	**$\nu_s(COO)$**	**$\beta_s(COO)$**	**$\beta_{as}(COO)$**	**19a**	**19b**	**18a**	**17a**	**14**	**11**	**9a**	**8a**	**8b**	**7a**	**6b**	**4**	**3**
								***o*-methoxybenzoic [22]**												
Acid	IR	2981	2951					1436	1492	1088	862		761	1152	1578	1599	1271		699	1287
	Raman	2982	2953					1437	1493	1096			761		1581	1600	1285		702	1285
Na	IR	2977	2944	1574	1404	851	513	1438	1487	1101			752	1151	1589	1612	1275	660		1296
	Raman	2978	2943	1577	1417			1441	1487	1102				1152	1597		1280	661		1299
Cu	IR	2964	2936	1566	1395	852	493	1437	1486	1105			765	1151	1589	1605	1274	670	706	1297
	IR_{ATR}			1574	1393	851		1427		1103						1597	1285	665	708	1300
								***m*-methoxybenzoic [22]**												
Acid	IR	2961	2877					1430	1490	1088	907	1324	754		1584	1606			679	1311
	Raman	2951						1430			907	1325	749		1587	1605			680	
Na	IR	2942		1563	1409	813	577		1486		900		758			1600	1282	501	678	1315
	Raman	2944		1576	1419	814			1486		901					1601	1282	502		1316
Cu	IR	2930		1555	1395	834		1425	1491	1084	918	1321	758		1582	1607	1283		671	1321
	IR_{ATR}			1568	1398	822	575			1082		1223					1287		674	
								***p*- methoxybenzoic [22]**												
Acid	IR	2986	2941					1517				1324	773	1168	1604	1577		633	697	
	Raman	2985	2942							1012		1323	775	1180	1610	1581		635	699	
Na	IR	2954	2935	1545	1421	841	535	1515				1314	778	1143	1612	1597		635	694	
	Raman	2954	2939	1568				1518				1319	775	1146	1616			636	696	
Cu	IR	2956	2936	1558	1400	849		1512				1310	779			1607		640	698	
	IR_{ATR}			1560	1395	849				1101		1310	779			1600		631	700	
		$\nu_{as}(NO_2)$	**$\nu_s(NO_2)$**	**$\nu_{as}(COO)$**	**$\nu_s(COO)$**	**$\beta_s(COO)$**	**$\beta_{as}(COO)$**	**19a**	**19b**	**18a**	**18b**	**14**	**11**	**9a**	**8a**	**8b**	**7a**	**6b**	**4**	**1**
								***o*-nitrobenzoic**												
Acid	IR	1532	1352					1488	1446	1073	1007	1308		1172	1577	1610	1263		691	678
[23]	Raman	1533	1369					1490	1446	1078	1004	1307		1173	1580	1608	1270		684	
Na	IR	1529	1356	1568	1399	839	582	1476	1438	1074	989	1306	803	1167	1589	1607	1262			648

Continued **Table 1.** Wavenumbers [cm^{-1}] of selected bands from the FT-IR and FT-Raman spectra of *o*-, *m*- and *p*-AM, MB and NB acids as well as their complexes with copper(II) and sodium ions.

		$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	$\nu_{as}(COO)$	$\nu_s(COO)$	$\beta_s(COO)$	$\beta_{as}(COO)$	19a	19b	18a	18b	14	11	9a	8a	8b	7a	6b	4	1
***o*-nitrobenzoic**																				
[24]	Raman	1528	1345	1573	1413	842	580	1480	1441	1075			802	1170	1608		1266			650
Cu	IR	1530	1353	1577	1413			1487		1077	991	1311	780		1612	1639	1267			651
	IR$_{ATR}$	1526	1346	1574	1410	843	583	1487		1078	989	1308	779		1611		1265			654
***m*-nitrobenzoic**																				
Acid	IR	1531	1359					1483	1450	1071	1085	1098	810	1152	1585	1616				662
[25]	Raman	1529	1350					1481	1437		1085	1100	804	1155	1584	1619				
Na	IR	1523	1350	1570	1397	907	509	1476	1431	1076		1097	790		1606	1615			653	669
[25]	Raman	1530	1349	1568	1402	910	501	1480	1438	1068	1088		796		1596	1614			653	
Cu	IR	1541	1348	1567	1414	913	484	1481	1436		1083		786			1608			657	668
	IR$_{ATR}$	1531	1348	1531	1404	922		1483			1084		783			1605				660
***p*-nitrobenzoic**																				
Acid	IR	1543	1353					1495	1430	1014	1110	1312		1198	1585	1608	1127	627	649	
[26]	Raman	1543	1358					1493	1442	1015	1109				1584	1599	1131	629		
Na	IR	1590	1352	1525	1408	833	514	1491	1396	1016	1105	1318		1172		1622	1139	626	670	
[26]	Raman		1353	1521	1426	835	517	1491	1405	1019				1182	1598	1625	1142	627	711	
Cu	IR	1570	1349	1528	1412	833	520			1013	1107	1320		1172	1599	1626	1144	633	669	
	IR$_{ATR}$	1578	1346	1522	1410	831				1016	1105			1182			1142	621	687	

to 145 cm^{-1} and it was slightly higher than $\Delta\nu(COO^-)$ obtained for sodium *p*-AB (134 cm^{-1}). Additionally, the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands from the IR spectra of copper(II) *p*-AB moved in the direction of lower wavenumbers compared with the spectrum of sodium *p*-AB. This suggests that in the molecule of copper(II) *p*-AB, the monodentate or bidentate bridging type of coordination exists. Only one literature example of crystallographic data for copper(II) aminobenzoate was found [14]. In the polymeric anhydrous structure of copper(II) *o*-AB, bridging structure of the carboxylate group exists (Fig. 2). Different types of metal ion coordination for copper(II) *o*-AB molecule may be caused by the form of studied compound, *i.e.*, literature data were obtained for crystal form, whereas in this work, a powder structure was examined.

Copper(II) complex formation causes changes in the electronic charge distribution in the aromatic ring of aminobenzoates. This entailed an alteration in the location of aromatic band vibrations in the spectra of complexes in comparison with the spectra of ligand. Namely, in the IR and Raman spectra of copper(II) complex, bands no. 18b, 5, 4, 6a, 16b (*o*-AB);. 13, 9b, 18b, 7b, 10a, 6a (*m*- AB); 19a, 19b, 7a, 10a, and 1 (*p*-AB) were considerably (>10 cm^{-1}) shifted in comparison with corresponding bands in the spectra of aminobenzoic acids.

On the basis of IR spectra of copper(II) and sodium methoxybenzoates, one may suppose that in copper(II) *o*-MB, the carboxylate group is bidentate bridging (Cu - $\Delta\nu(COO^-)$=171 cm^{-1}, Na - $\Delta\nu(COO^-)$=170 cm^{-1}; $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands were shifted toward lower wavenumbers in the spectrum of the copper complex compared with the spectrum of sodium salt). Literature crystallographic data for copper(II) *o*-MB were found that show bidentate bridging structure of the carboxylate group as well in this molecule (Fig. 3) [15]. However, it should be noted that in this work, the anhydrous structure was studied, whereas the literature data concern the hydrated compound. For copper(II) *m*-MB, the value of $\Delta\nu(COO^-)$ was 160 cm^{-1} [sodium salt: $\Delta\nu(COO^-)$=154 cm^{-1}], and the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands were located at lower wavenumbers compared with the spectrum of sodium *m*-MB. The small difference between the values of $\Delta\nu(COO^-)$ for copper(II) and sodium compounds points to bidentate bridging or monodentate character of the carboxylate group in copper *m*-MB. In the IR spectrum of copper(II) *p*-MB, the $\nu_{as}(COO^-)$ band was shifted to higher wavenumbers and $\nu_s(COO^-)$ to lower wavenumbers in comparison with the locations of these bands in the spectrum of sodium *p*-MB. Moreover, values of $\Delta\nu(COO^-)$ amounted to 158 cm^{-1} and 124 cm^{-1} for copper(II) and sodium *p*-MB, respectively. These data suggest that the copper ion is coordinated by a monodetate carboxylate group in the *p*-MB molecule.

In the series of spectra of compounds (methoxybenzoic acid → sodium methoxybenzoate → copper(II) methoxybenzoate), the displacement of bands assigned to the stretching vibration of methoxy group – $\nu_{as}(CH_3)$ – toward lower wavenumbers was observed. It showed that the oxygen atom from the –OCH_3 group takes part in copper ion coordination.

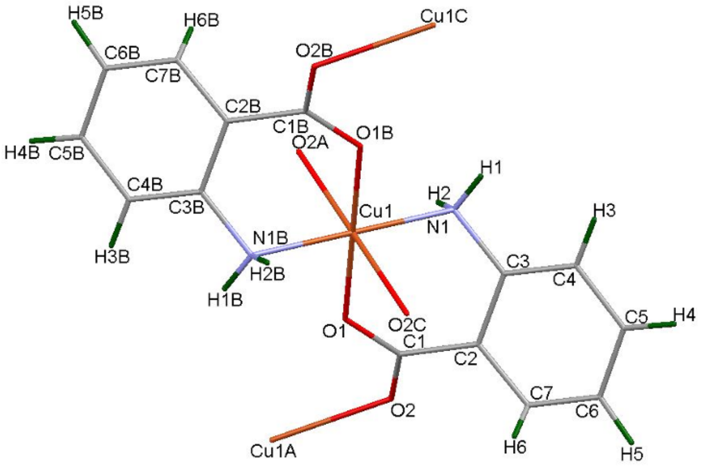

Figure 2. Crystal structure of catena(bis(o-aminobenzoato-copper(II))) [14].

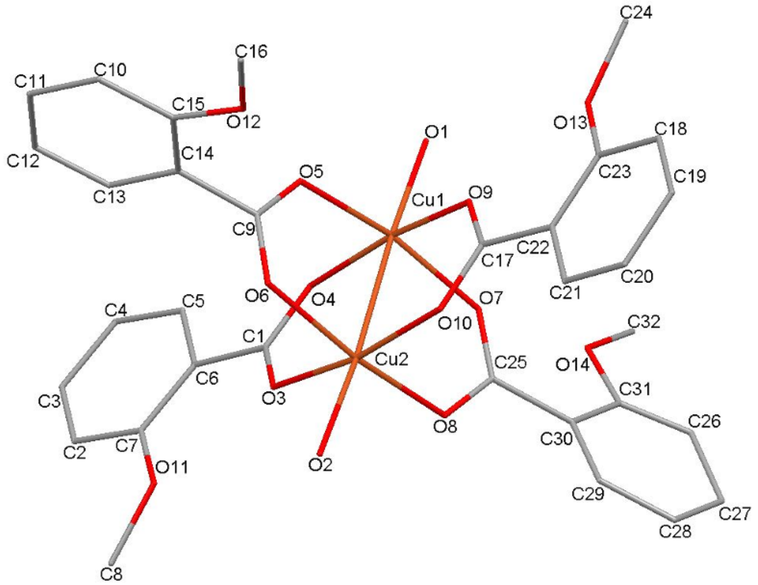

Figure 3. Crystal structure of bis(aqua-bis(μ_2-2-methoxybenzoato-O,O')-copper(II)) [15].

Moreover, one can see visible changes in the location of bands derived from aromatic ring vibrations in the spectra of complexes compared with the spectra of acid. Specifically, the bands no. 3, 18a, 6a (copper *o*-MB), 14, 18a, 17a, 11, 6b (copper *m*-MB) and 14, 18a, 17a, 11, 6b (copper *p*-MB) underwent movement of more than 10 cm^{-1} in the spectra of methoxybenzoates, compared with the spectra of acid.

Using spectroscopic criteria, the following type of metal coordination in copper(II) nitrobenzoates may be proposed: bidentate bridging in copper *o*-NB (Cu - $\Delta\nu(COO^-)$=164 cm^{-1}, Na - $\Delta\nu(COO^-)$=169 cm^{-1}), bidentate chelating in copper *m*-NB (Cu - $\Delta\nu(COO^-)$= 153 cm^{-1}, Na - $\Delta\nu(COO^-)$=173 cm^{-1}; bands of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in IR spectra of Cu complex are shifted to lower and higher wavenumbers, respectively) and bidentate bridging in copper *p*-NB (Cu - $\Delta\nu(COO^-)$=116 cm^{-1}, Na - $\Delta\nu(COO^-)$=117 cm^{-1}; bands of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in IR spectra of Cu complex are shifted to higher wavenumbers). The crystal data for copper *o*- and *p*-NBs revealed bridging structure of the carboxylate group (Figs. 4 and 5) [16-18], which confirms the assumption that relied on the location of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in IR spectra of Cu complex and sodium salt.

It should be stressed that spectroscopic criteria should be applied with caution. For example, in the FT-IR spectra of binary palladium carboxylates, $Pd_3(\mu\text{-}RCO_2)_6$, the values of $\Delta\nu(COO^-)$ vary from 160 to 200 cm^{-1} (depending on R) but the type of coordination remains the same (*i.e.*, bridging coordination evidenced from X-ray data) [19]. Another example – on the basis

Table 2. The values of magnetic susceptibilities and magnetic moments for copper(II) aminobenzoates calculated in the range of 76-303 K.

Temp. [K]	Magnetic susceptibility $[cm^3\ mol^{-1}]$			Magnetic moment $[\mu_\beta]$		
	Cu(II) aminobenzoates					
	o-	*m-*	*p-*	*o-*	*m-*	*p-*
76	5020	5112	5248	1.78	1.79	1.82
123	2838	2926	2794	1.72	1.75	1.71
133	2596	2658	2544	1.72	1.74	1.71
143	2384	2454	2354	1.71	1.73	1.71
153	2217	2265	2203	1.71	1.73	1.71
163	2080	2141	2093	1.71	1.74	1.72
173	1970	2022	1963	1.72	1.74	1.73
183	1882	1923	1883	1.73	1.75	1.74
193	1789	1843	1793	1.74	1.77	1.75
203	1706	1729	1713	1.74	1.76	1.76
213	1626	1694	1638	1.75	1.78	1.76
223	1556	1595	1567	1.75	1.78	1.77
233	1494	1545	1492	1.76	1.79	1.77
243	1432	1480	1442	1.76	1.79	1.78
253	1380	1431	1377	1.77	1.80	1.78
263	1322	1381	1327	1.77	1.81	1.79
273	1283	1351	1307	1.78	1.81	1.79
278	1252	1361	1252	1.78	1.85	1.79
288	1225	1282	1227	1.79	1.83	1.81
303	1164	1237	1172	1.80	1.85	1.82

Table 3. The values of magnetic susceptibilities and magnetic moments for copper(II) metoxybenzoates calculated in the range of 76-303 K.

Temp. [K]	Magnetic susceptibility $[cm^3\ mol^{-1}]$			Magnetic moment $[\mu_\beta]$		
	Cu(II) methoxybenzoates					
	o-	*m-*	*p-*	*o-*	*m-*	*p-*
76	188	2562	2904	0.47	1.29	1.37
123	534	2104	1975	0.84	1.50	1.46
133	585	2015	1848	0.90	1.53	1.47
143	633	1964	1767	0.96	1.57	1.49
153	665	1913	1686	1.02	1.60	1.51
163	677	1869	1599	1.06	1.63	1.52
173	695	1818	1553	1.10	1.66	1.55
183	728	1761	1490	1.15	1.68	1.56
193	740	1723	1449	1.19	1.71	1.58
203	734	1672	1403	1.22	1.73	1.60
213	737	1634	1363	1.25	1.76	1.62
223	740	1576	1305	1.28	1.77	1.63
233	734	1551	1265	1.30	1.80	1.64
243	725	1513	1224	1.32	1.81	1.65
253	725	1481	1190	1.35	1.83	1.66
263	722	1443	1161	1.38	1.85	1.68
273	746	1411	1143	1.42	1.86	1.70
278	716	1392	1109	1.41	1.87	1.69
288	710	1367	1091	1.43	1.89	1.71
303	701	1328	1045	1.46	1.91	1.72

of FT-IR spectra recorded for anhydrous bidentate bridging zinc acetate and hydrated bidentate chelating zinc acetate, the values of $\Delta\nu(COO^-)$ are 118 cm^{-1} and 113 cm^{-1}, respectively. Ishioka *et al.*, proposed to examine the deforming vibrations of the carboxylate anion – $\beta(COO^-)$ – as an additional parameter to $\Delta\nu(COO^-)$ [7]. In the case of aminobenzoates, methoxybenzoates and nitrobenzoates, there is no distinct relationship between the type of coordination and the value of $\Delta\beta(COO^-)$. For example, for *p*-amino-, *o*-methoxy- and *m*-nitrobenzoates the values of $\Delta\beta(COO^-)$ are lower for sodium salts than for copper(II) complexes (the differences between $\Delta\beta(COO^-)_{Cu\ complex}$ and $\Delta\beta(COO^-)_{Na\ salt}$ are equal to: 24, 21 and 31 cm^{-1}), but the type of metal ion coordination for these three compounds is different.

In the FT-IR spectra, *o*-nitrobenzoates and nitrobenzoic acid bands of $–NO_2$ group vibrations are located at similar wavenumbers. However, in the spectra of *m*- and *p*-nitrobenzoates, bands assigned to $–NO_2$ vibrations, especially the $\nu_{as}(NO_2)$ band, undergo distinct movement compared with the spectrum of nitrobenzoic acids. The differences between the location of $\nu_{as}(NO_2)$ in the spectra of *p*-nitrobenzoates and *p*-nitrobenzoic acid are: 47 cm^{-1} (Na) and 27 cm^{-1} (Cu). It suggests that *p*-NBA molecules participate in strong hydrogen bonds that are broken when complexes are formed. Comparing the position of bands derived from aromatic ring vibrations, one may observe the changes in the electronic charge distribution in molecules caused by ionic and covalent bond formation in sodium salt and copper complex, respectively. This tendency is more visible in the spectrum of sodium *o*-NB than *m*- and *p*-NBs. Among bands that are significantly shifted toward lower wavenumbers (or disappear) in the spectra of sodium *o*-, *m*- and *p*-nitrobenzoates compared with the spectrum of appropriate nitrobenzoic acids are: 19a, 19b, 18a and 9a. However, comparing the spectra of copper(II) nitrobenzoates and nitrobenzoic acids, the most significant changes (>10 cm^{-1}) are observed in the location of the following bands: 18b, 13, 8b and 1 (*o*-NB); 19b and 11 (*m*-NB); 9a, 8a, 8b, 7a and 4 (*p*-NB).

The effect of copper and sodium ions on the electronic charge distribution in the aromatic ring is weak. Number, wavenumbers and intensity of corresponding bands derived from aromatic ring vibrations in the IR and Raman spectra of copper and sodium compounds as well as ligand do not differ significantly from each other. After further detailed analysis of these slight differences some systematic changes can be observed. Coordination of the copper ion to the studied ligands caused smaller perturbation of the electronic charge distribution in the aromatic ring than formation of sodium salt. Number, wavenumbers and intensity of most of the

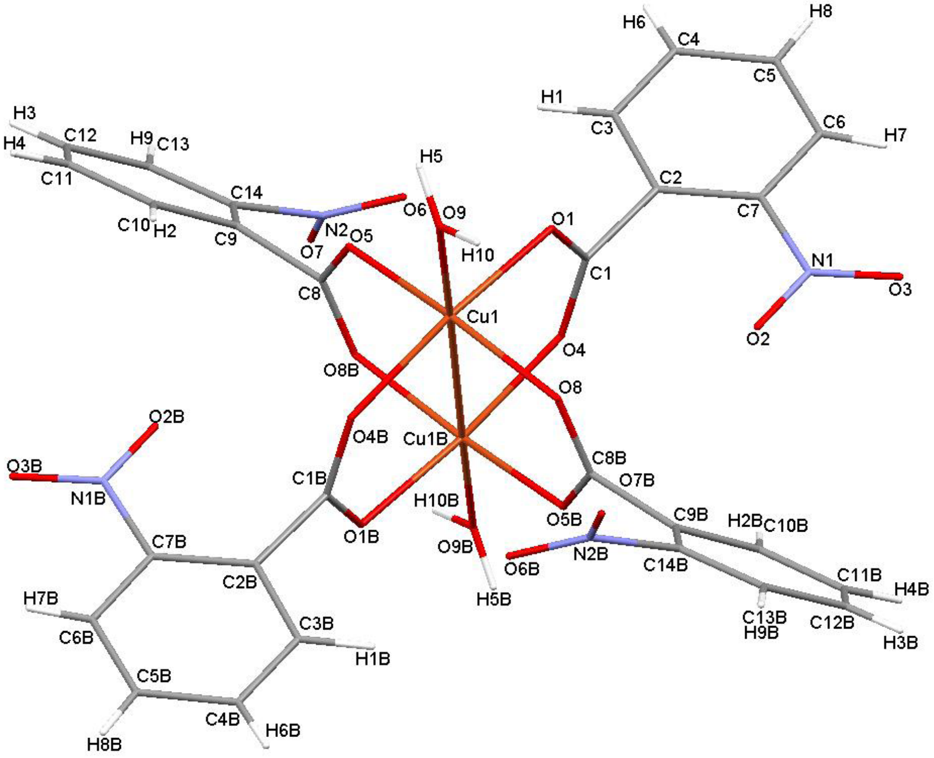

Figure 4. Crystal structure of tetrakis(μ_2-2-nitrobenzoato-O,O')-diaqua-di-copper(II) [17].

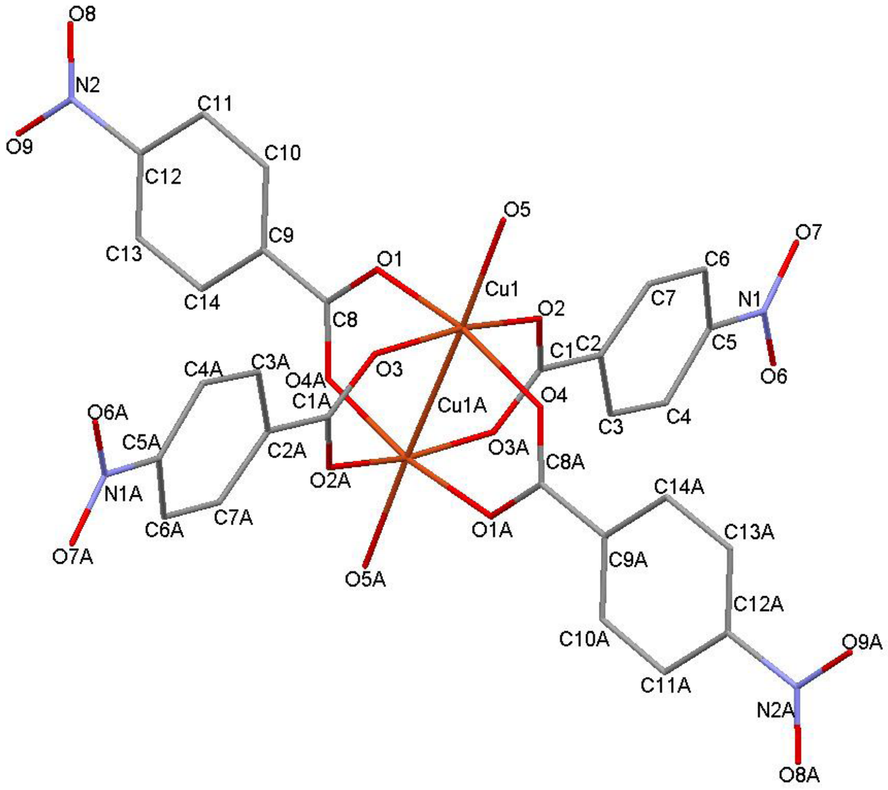

Figure 5. Crystal structure of diaqua-tetrakis(μ_2-p-nitrobenzoato-O,O')-di-copper dihydrate [18].

bands assigned to the aromatic ring vibrations is higher (and similar to that in the spectra of ligand) for copper complexes than sodium salts. The sodium ion forms an ionic bond with the ligand whereas copper(II) ion forms a partially covalent bond. Formation of bidentate bridging and bidentate chelating structures with copper(II) ion (like in case of MB and NB molecules) is related to higher symmetrization of the electronic charge in the carboxylate anion (in comparison with the ionic and monodentate structures in sodium salts). Higher symmetrization of the bidentate chelating structure as compared to monodentate results from the equalization of bond order in the carboxylate group. Therefore, in case of complexes with copper(II) ion (in comparison with sodium salts), a higher delocalization of the electronic charge distribution in the aromatic ring together with more uniform distribution of electronic charge in the carboxylate anion can occur. On the other hand, formation of an ionic bond (which is connected with a division of the electronic charge in COO^- like in sodium salts) caused a perturbation of the electronic system in the aromatic ring.

Similar, but more distinct changes were observed in our other papers [27-29]. Studies on different complexes with carboxylic aromatic acids revealed that metal ions with small ionic potential (the ratio of an ion charge to its radius) like Ag(I), Hg(I), Hg(II), Cd(II), alkali metal ions disturb the uniform electronic charge distribution in the aromatic ring whereas metal ions with high ionic potential, like Cr(III), Fe(III), Y(III), Al(III) and Ln(II), stabilize it. Delocalization of the electronic charge in ‘d’ and ‘f’ orbitals (3d element and lanthanide ions) favours delocalization of the electronic charge in the carboxylic group and delocalization of the π electrons in the aromatic ring. On the contrary, formation of the ionic bond between alkali metal ions and the carboxylic anion causes bond polarization, division of the electronic charge and perturbation of the aromatic system.

3.2. Magnetic studies

The interpretation of magnetic measurement results allows the mono- and dimeric structures of compounds to be distinguished [19,20]. The monomeric molecules of Cu(II) compouds typically have magnetic moment values greater than 1.7 μ_β while for those in the dimer form, the values are less than 1.7 μ_β (Tables 2 and 3). Moreover, for the monomeric Cu(II) complexes the magnetic susceptibility values decrease with the increase of temperature, what is conversely than in case of their dimers.

The dependence of molar magnetic values of the complexes with temperature gives information about the paramagnetic nature of interactions between complex centres. When the magnetic susceptibility values of central ions decrease with decreasing temperature, antiferromagnetic interactions appear, whereas an increase in susceptibility with decreasing temperature points to ferromagnetic interactions. The course of the curves of magnetic susceptibility values with temperature for *o*-methoxybenzoate of Cu(II) indicates its dimeric structure. Its magnetic moment values change from 0.47 μ_β (76 K) to 1.47 μ_β (303 K), and between magnetic centres, the antiferromagnetic interaction appears. The carboxylate group is a bidentate ligand. From the dependence of magnetic moment values on temperature for *m*- and *p*-methoxybenzoates of Cu(II), it follows that they are monomers with ferromagnetic interactions between magnetic centres. The values of magnetic moments for these complexes, calculated in the range of 76-303 K, change from 1.29 μ_β (76 K) to 1.91 μ_β (303 K) for *m*-methoxybenzoate of Cu(II) and from 1.37 μ_β (76 K) to 1.72 μ_β (303 K) for *p*-methoxybenzoate of Cu(II) (Table 3). Similarly, the values of magnetic susceptibilities and the magnetic moments for *o*-, *m*- and *p*-aminobenzoates of Cu(II) indicate also their monomeric structures and the ferromagnetic interaction between magnetic centres (Table 2). The magnetic moment values calculated for those compounds are similar, in the range of 1.78 μ_β (76 K)-1.85 μ_β (303 K). From the analysis of the obtained data it follows that *o*-methoxybenzoate of Cu(II) belongs to the molecular antiferromagnets. The properties of antiferromagnets result from the magnetic superexchange between two Cu(II) centres being conjugated by bridged carboxylate groups. As a consequence of the spin-spin coupling in these complexes on the Cu(II) centres, two states – singlet and triplet – are formed [19-21]. Singlet or triplet states describe the electronic multiplicity expressed by the formula 2S+1, in which S is the spin number for all electrons in atom taking values: 0, 1/2, 1, 3/2 and 2. Therefore when S=0, then 2S+1=1 indicates the singlet state which means that electrons in the atom are paired. The doublet state takes place when S=1/2. It is typical for atoms having one unpaired electron. When S=1, then the triplet state typical for atoms with two unpaired electrons appears. The singlet-triplet energetic interval is equal to the double exchange parameter *J* value. The exchangeable interaction of the two metallic ions with half spins is described by the Heisenberg-Dirac-Van Vleck Hamiltonian [20,21]. In the dimer Cu(II) carboxylate, the singlet-triplet energetic interval value is comparable with kT (k-Boltzman constant, T-absolute temperature) which indicates that not all Cu(II) ions are in the ground state; some are in the excited ones. Therefore, in the Cu(II) dimer in the higher temperatures, the electrons occupying both singlet and triplet states are placed mainly in the latter. The dimer magnetic moment value for one magnetic centre is within the range of 0-1.73 μ_β. The magnetic moment value reaches its maximum at room temperature. With its lowering, the filling of the triplet state decreases, and, in the sufficiently low temperature typical for dimer, it shows the magnetic moment value being equal to 0. *o*-Methoxybenzoate of Cu(II) belongs to the molecular antiferromagnets. The electron distributions in the ligand in this type of complex depend on the number of unpaired electrons of the metal. The bond between metal orbitals containing only one unpaired electron and the pure *p* orbital of ligand consists of the pairing of the unpaired electron of the first metal with that of opposite spin in the *p* orbital. The pairing of the second electron in the *p* orbital with a *d* electron of the second metal takes place when that last one has an opposite spin compared to the *d* of the first metal. As a result, the two metal ions are antiferromagnetically conjugated by ligand.

o-, *m*- and *p*-Nitrobenzoates of Cu(II) show paramagnetic properties. Only *m*-nitrobenzoate of Cu(II) obeys the Curie-Weiss law, since the values of its magnetic susceptibility decrease with increasing temperature. Its values of magnetic moments change from 2.37 μβ (76 K) to 2.30 μβ (303 K). This complex seems to be a monomer. From the analysis of data obtained for *o*- and *p*-nitrobenzoates of Cu(II) it appears that they are dimers with antiferromagnetic interactions. Their magnetic susceptibility values decrease with decreasing temperature. The values of magnetic moments for *o*-nitrobenzoate of Cu(II) are in the range of 0.45 μβ (76 K) – 1.90 μβ (303 K), and for *p*-nitrobenzoate of that element they change from 0.82 μβ (76 K) to 1.67 μβ (303 K).

4. Conclusion

On the basis of spectroscopic and magnetic data the following conclusions are derived:

(1) Copper ion tends to form with amino-, methoxy and nitrobenzoate ligands monodentate structures (copper AB), bidentate bridging (copper *o*-MB and *o*- and *p*-NB) as well as bidentate chelating (copper *m*-NB), whereas for sodium salts, ionic or monodentate structures dominate.

(2) Copper ion can coordinate amino-, methoxy and nitrobenzoates also through functional groups, especially $-NH_2$, as well as $-OCH_3$ and $-NO_2$. This was proved by considerable changes in the wavenumbers of bands assigned to the mentioned groups in the IR and Raman spectra of appropriate acids and salts.

Magnetic study revealed that in the copper(II) *o*-methoxybenzoate, the antiferromagnetic interaction appears between magnetic centres, nitrobenzoates of Cu(II) show paramagnetic properties, while the other copper(II) complexes show them as ferromagnetic.

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