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THERMAL, SPECTRAL AND MAGNETIC CHARACTERIZATION OF Co(II), Ni(II) AND Cu(II) 4-CHLORO-2-NITROBENZOATES

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Physico-chemical properties of 4-chloro-2-nitrobenzoates of Co(II), Ni(II), and Cu(II) were studied. The complexes were obtained as mono- and trihydrates with a metal ion to ligand ratio of 1:2. All analysed 4-chloro-2-nitrobenzoates are polycrystalline compounds with colours depending on the central ions: pink for Co(II), green for Ni(II), and blue for Cu(II) complexes. Their thermal decomposition was studied only in the range of 293–523 K, because it was found that on heating in air above 523 K 4-chloro-2-nitrobenzoates decompose explosively. Hydrated complexes lose crystallization water molecules in one step and anhydrous compounds are formed. The final products of their decomposition are the oxides of the respective transition metals. From the results it appears that during dehydration process no transformation of nitro group to nitrite takes place. The solubilities of analysed complexes in water at 293 K are of the order of 10^{-4}–10^{-2} mol dm^{-3}. The magnetic moment values of Co^{2+}, Ni^{2+} and Cu^{2+} ions in 4-chloro-2-nitrobenzoates experimentally determined at 76–303 K change from 3.89 to 4.82 μ_B for Co(II) complex, from 2.25 to 2.98 μ_B for Ni(II) 4-chloro-2-nitrobenzoate, and from 0.27 to 1.44 μ_B for Cu(II) complex. 4-chloro-2-nitrobenzoates of Co(II), and Ni(II) follow the Curie–Weiss law. Complex of Cu(II) forms dimer.

Keywords: *4-chloro-2-nitrobenzoates, complexes of Co(II), Ni(II) and Cu(II), IR spectra, magnetic moments, thermal stability*

Introduction

4-Chloro-2-nitrobenzoic acid is a light-yellow crystalline solid sparingly soluble in water. Its electrolytic dissociation constant is equal to $1.0\cdot10^{-2}$ (25°C) and melting point 140°C [1]. The compounds of 4-chloro-2-nitrobenzoic acid anion are very little known. A survey of the literature shows that it is possible to find papers on the complexes of various ligands with some of *d* block elements [2–7] and also on their salts with 4-chloro-2-nitrobenzoic acid anion. The salts of 4-chloro-2-nitrobenzoic acid anion were obtained in the solid state only with the cations: NH_4^+, Na^+, K^+, Ag^+, Cu^{2+}, Ca^{2+}, Ba^{2+}, and with rare-earth elements [1, 8]. 4-chloro-2-nitrobenzoate of Cu(II) was obtained in the solid state as trihydrate with light-green colour [1]. Moreover some complexes of transition element cations with various isomers of chloronitro- and chloromethoxybenzoic acid anions were also prepared as solids and investigated [8–15]. The 4-chloro-2-nitrobenzoates of Co(II) and Ni(II) have not been obtained so far. Therefore the aim of this work was to prepare them in the solid state, and also that of Cu(II), and to examine some of their physico-chemical properties including thermal stability in air during heating to 523 K, IR spectral characterization, X-ray powder investigations, solubility in water at room temperature, and magnetic behaviour at 76–303 K. Thermal stability investigations give informations about the process of dehydration. The magnetic susceptibility measurements let study the kinds of the way of coordination of the central ions, and the nature of the bonding between central ions, and ligands. If the magnetic moment is known, the number of unpaired electrons can be calculated. This may also give information on the oxidation state of the central metal ion of a complex. When the number of unpaired electrons on the ion of complex is known the spin-only moment can be calculated. The deviation of the measured magnetic moment from the spin-only permits the drawing of conclusion on the symmetry of the complex in certain cases. The determination of the number of unpaired electrons on the central atom establishes whether the complex investigated is of low or high spin or the ligands form the strong or weak fields.

Experimental

The 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were prepared by adding the equivalent quantities of 0.1 M ammonium 4-chloro-2-nitrobenzoate (pH≈5) to a hot solution containing the Co(II), Ni(II) and Cu(II) chlorides and crystallizing at 293 K. The solids formed were filtered off, washed with hot water and methanol to remove ammonium ions, and dried at

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303 K to a constant mass. The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyzer. The content of chloride was determined by the Schöniger method. The contents of metals were established by ASA method with the use of ASA 880 spectrophotometer (Varian).

The IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using M-80 spectrophotometer (Carl Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs.

The X-ray powder diffraction patterns were performed on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered CuK_{α} radiation. The measurements were made within the range of $2\theta=4–80°$ by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 TG, DTG and DSC instrument. The experiments were carried out under air flow in the temperature range of 293–523 K. Samples ranging from 5.19 mg (Co), 5.18 mg (Cu) to 5.06 mg (Ni) were heated in Al_2O_3 crucibles.

The thermal stability and decompositions of the prepared chloronitrobenzoates were determined by Paulik–Paulik–Erdey θ-1500D derivatograph with Derill converter, recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples (100 mg) were heated in platinum crucibles in static air to 523 K with a TG sensitivity equal to 100 mg. DTG and DTA sensitivities were regulated by computer Derill programme. The products of decomposition were calculated from TG curves and verified by the X-ray diffraction pattern.

The solubilities of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in water were measured at 293 K. Saturated solutions of the obtained compounds were prepared under isothermal conditions. The contents of Co(II), Ni(II) and Cu(II) were determined using ASA 880 spectrophotometer (Varian).

Magnetic susceptibilities of polycrystalline samples of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were investigated at 76–303 K. The measurements were carried out using the Gouy method with magnetic field strength of 9.9 k0e. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrant employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibilities was assumed to be $1.644\cdot10^{-5}$ cm^3 g^{-1}. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [16, 17]. Magnetic moments were calculated according to Eq. (1):

$$\mu_{eff}=2.83(\chi_M T)^{1/2} \qquad (1)$$

Results and discussion

4-Chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were obtained as polycrystalline solids with a metal ion to ligand ratio of 1:2, and general formula $M(C_7H_3O_4NCl)_2\cdot nH_2O$ (where M=Co, Ni, Cu, and n=3 for Co and Ni, n=1 for Cu), and colours: pink for Co(II), green for Ni(II) and blue for Cu(II) complexes (Table 1).

Some of the results of IR spectra analysis are in Table 2. The infrared spectrum of 4-chloro-2-nitrobenzoic acid shows the following absorption bands [18–21]: a strong band of COOH at 1710 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of NO_2 group at 1530 and 1350 cm^{-1}, the bands

Table 1 Elemental analysis data of Co(II), Ni(II) and Cu(II) 4-chloro-2-nitrobenzoates

Complex $L^-=C_7H_3O_4NCl$	H/%		C/%		Cl/%		N/%		M/%	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$CoL_2\cdot3H_2O$	2.33	2.35	32.68	32.33	13.80	13.80	5.45	5.30	11.46	11.40
$NiL_2\cdot3H_2O$	2.34	2.48	32.70	32.19	13.82	13.84	5.45	5.40	11.42	11.30
$Cu_2L_4\cdot2H_2O$	1.66	1.51	34.81	34.87	14.71	14.71	5.80	5.78	13.16	13.10

Table 2 Wavenumbers (cm^{-1}) of COO^- bands in 4-chloro-2-nitrobenzoates of Co(II), Ni(II), Cu(II) and Na(I) and of the COOH band in 4-chloro-2-nitrobenzoic acid

Complex $L^-=C_7H_3O_4NCl$	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\Delta\nu_{OCO}$	$\nu_{C–Cl}$	$\nu_{M–O}$
$CoL_2\cdot3H_2O$	–	1590	1400	190	740	500
$NiL_2\cdot3H_2O$	–	1590	1400	190	740	490
$Cu_2L_4\cdot2H_2O$	–	1620	1420	200	750	540
HL	1710	–	–	–	–	–
NaL	–	1625	1400	225	760	440

of ν_{C-C} vibrations at 1610, 1425, 1150 and 1110 cm^{-1}, the bands of ν_{C-H} vibrations at 3100, 900 and 810 cm^{-1}, and the bands of ν_{C-Cl} stretching vibrations at 740 cm^{-1}. The bands of skeleton vibrations occur at 620 and 570 cm^{-1} [18–21].

In the IR spectra of 4-chloro-2-nitrobenzoates the band at 1710 cm^{-1} disappears, which confirms that no COOH is present in the complexes. In these spectra the intense broad absorption bands at 3570–3400 cm^{-1} confirm the presence of crystallization water. The bands arising from asymmetric and symmetric vibrations of COO^- group occur at 1620–1590 and 1420–1400 cm^{-1}, respectively. The bands at 1540–1530 and 1360–1350 cm^{-1} are assigned to asymmetric and symmetric vibrations of the NO_2 group. They are not significantly shifted with respect to those of the parent acid, and thus one must conclude that the NO_2 group is not coordinated to the metal ions. The ν_{C-Cl} stretching vibration occurs at 750–740 cm^{-1}, and the bands at 540–490 cm^{-1} are assigned to the metal–oxygen ionic bond. The bands of skeleton vibrations are shifted to lower frequencies (600 and 550 cm^{-1}) compared to those in the acid IR spectrum. The changes in their positions are caused by the interaction between aromatic ring vibrations and the groups of atoms and ions. In the IR spectra of the complexes the bands of $\nu_{as(OCO^-)}$ are shifted to lower frequencies whereas the bands of $\nu_{s(OCO^-)}$ are moved to higher or stay at the same frequencies compared to those of the sodium salt (Table 2). Therefore it is possible to assume that the carboxylate ion is a bidentate, chelating group [18, 22, 23]. The magnitudes of separation, $\Delta\nu_{OCO^-}$ between the frequencies due to $\nu_{as(OCO^-)}$, and $\nu_{s(OCO^-)}$ in the analysed complexes indicate a lower degree of ionic bond in these compounds compared to sodium salt. Having a greater ionic potential than a sodium ion, Co^{2+}, Ni^{2+} and Cu^{2+} ions have a stronger deforming effect on the ligand.

In order to verify that the prepared complexes are not converted to the nitrite isomers (during precipitation or on heating to 523 K), the IR spectra of the hydrates of 4-chloro-2-nitrobenzoates, and of dehydrated complexes, and also of sodium nitrite were recorded. A survey of the literature shows that under the influence of sunlight or with rising the temperature the nitro complexes may be transformed to the nitrite analogues in the endothermic process [24]. It was found that the isomerization of the nitro group may accompany the dehydration process of the complex or be connected with the transformation process in its inner sphere [25]. As a monodentate ligand, nitrite ion may be bounded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrite complex. The general effect of coordination via nitrogen is a rise in the frequencies of both $\nu_{as(NO_2)}$ and $\nu_{s(NO_2)}$ compared to the values for the free ion ~1328 and ~1260 cm^{-1}, respectively [26]. The IR spectra recorded for the hydrated, and dehydrated 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) show that the nitro group is not transformed to the nitrite group with rising temperature. No bands confirming the isomerization of the nitro group through the oxygen atom are observed [25, 26].

From the X-ray diffraction patterns recorded for the 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) it appears that they are crystalline of low symmetry and large size of the unit cells. They have different crystal structures [27], which have not been determined, because their single crystals have not been obtained so far.

It follows from earlier studies on the thermal stability of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) that on heating these complexes are explosively decomposed when heated above 523 K [28, 29]. The thermal stability of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) was studied in the range of 293–523 K. The results reveal that the analysed compounds lose the crystallization water in one step at 347–395 K. The process is connected with an endothermic effect as shown by the DTA curves [30–32].

The anhydrous 4-chloro-2-nitrobenzoates are formed above 380 K. The loss in mass calculated from TG curves is about 11% in the case of trihydrates, and 4% in the case of monohydrate of Cu(II) 4-chloro-2-nitrobenzoate (Table 3). Their theoretical values are 10.5 and 3.7%, respectively. Considering the temperatures at which the dehydration takes place and the way by which it proceeds it is possible to assume that the water molecules form outer sphere water [32]. The anhydrous complexes of Co(II), Ni(II) and Cu(II) are finally decomposed to the oxides of respective metals: CoO, NiO and CuO, which were

Table 3 Temperature range of the dehydration process of Co(II), Ni(II) and Cu(II) 4-chloro-2-nitrobenzoates in air atmosphere and their solubility in water at 293 K

Complex $L^-=C_7H_3O_4NCl$	ΔT/K	Mass loss/%		n	ΔH/kJ mol^{-1}	Solubility/mol dm^{-3}
		calcd	found			
$CoL_2\cdot 3H_2O$	361–395	10.5	11.0	3	108.07	$1.29\cdot 10^{-2}$
$NiL_2\cdot 3H_2O$	362–393	10.5	11.0	3	125.84	$6.62\cdot 10^{-4}$
$Cu_2L_4\cdot 2H_2O$	347–364	3.7	4.0	1	60.01	$4.70\cdot 10^{-4}$

ΔT – temperature range of dehydration process; n – the number of loss of water molecules; ΔH – enthalpy of dehydration process.

identified by IR spectra, and X-ray powder diffractograms. The product of the final decompositions of chloronitrobenzoates were obtained by roasting the analysed complexes of Co(II), Ni(II) and Cu(II).

The thermogravimetric studies of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were carried out with DSC/TG technique at 293–523 K (Table 3). The obtained results reveal the complexes to be hydrates containing three or one molecules of water of crystallization depending on the central ion. As example, the TG, DTG and DTA curves of Ni(II) 4-chloro-2-nitrobenzoate are presented in Fig. 1. The complexes are stable up to 300-350 K. Next in the range of 300–400 K they dehydrate in one step. The mass losses estimated from TG curves (3.8–10.9%) correspond to the loss from 1 to 3 molecules of water (the theoretical values are equal to 3.7–10.5%), and the energetic effect (ΔH=60.01–125.84 kJ mol^{-1}) accompanying these transformation processes confirm the losses of definitive numbers of water molecules. The products of dehydration process were also characterized by elemental analysis, IR spectra, and X-ray powder diffractograms.

The solubilities of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) in water at 293 K were measured (Table 3). They are in the order of 10^{-4}–10^{-2} mol dm^{-3}. The Co(II) 4-chloro-2-nitrobenzoate is the most soluble, while those of Ni(II) and Cu(II) the least soluble salts. From the obtained results it appears that 4-chloro-2-nitrobenzoic acid may be used as an eluent for the separation of transition metal ions by ion-exchange chromatography.

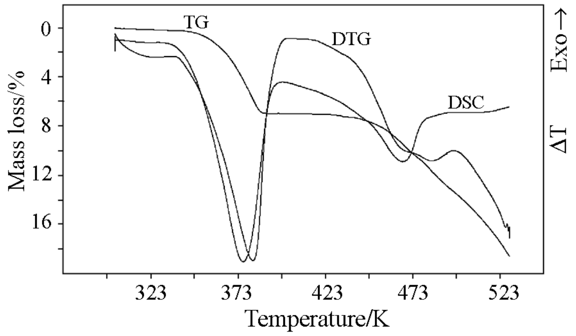

Fig. 1 TG, DTG and DSC curves of Ni(II) 4-chloro-2-nitrobenzoate

The magnetic susceptibility of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) was measured over the range of 76–303 K (Table 4). The measured values for Co(II) and Ni(II) complexes obey the Curie–Weiss law suggesting a weak ferromagnetic interaction (Fig. 2). The magnetic moment values experimentally determined at 76–303 K for Co(II) and Ni(II) compounds change from 3.89 μ_B (at 76 K) to 4.82 μ_B (at 303 K) for Co(II) complex, and from

Table 4 Values of μ_{eff} of 4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) [L^{-}=$C_7H_3O_4NCl$]

$CoL_2\cdot 3H_2O$			$NiL_2\cdot 3H_2O$			$Cu_2L_4\cdot 2H_2O$		
T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B	T/K	$\chi_M\cdot 10^6$	μ_{eff}/μ_B
76	24908	3.89	76	8344	2.25	76	117	0.27
123	18874	4.31	123	6645	2.56	123	405	0.63
133	17610	4.33	133	6268	2.58	133	478	0.71
143	16599	4.36	143	5983	2.62	143	536	0.78
153	15799	4.40	153	5759	2.66	153	608	0.86
163	15061	4.43	163	5566	2.70	163	671	0.94
173	14392	4.47	173	5316	2.71	173	710	0.99
183	13927	4.52	183	5133	2.74	183	749	1.05
193	13394	4.55	193	4955	2.77	193	768	1.09
203	12895	4.58	203	4802	2.79	203	802	1.14
213	12410	4.60	213	4634	2.81	213	826	1.19
223	11980	4.63	223	4487	2.83	223	836	1.22
233	11556	4.64	233	4344	2.85	233	846	1.26
243	11180	4.66	243	4217	2.86	243	855	1.29
253	10866	4.69	253	4110	2.89	253	865	1.32
263	10558	4.72	263	4003	2.90	263	870	1.35
273	10305	4.75	273	3912	2.92	273	841	1.36
283	10039	4.77	283	3952	2.99	283	865	1.40
293	9807	4.80	293	3744	2.96	293	855	1.42
303	9568	4.82	303	3657	2.98	303	860	1.44

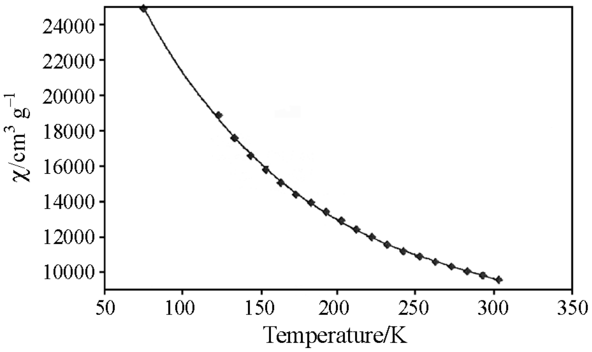

Fig. 2 Dependence between magnetic susceptibility values *vs.* temperatures for Co(II) complex

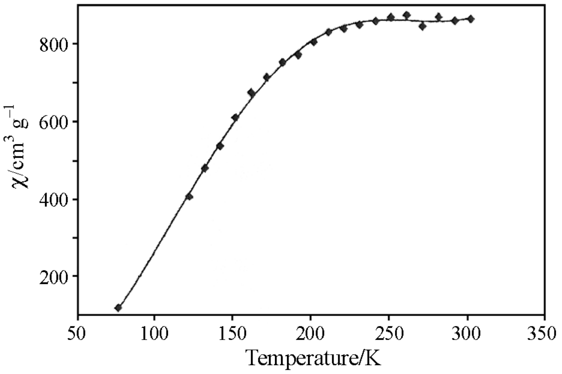

Fig. 3 Dependence between magnetic susceptibility values *vs.* temperatures for Cu(II) 4-chloro-2-nitrobenzoate

2.25 μ_B (at 76 K) to 2.98 μ_B (at 303 K) for Ni(II) 4-chloro-2-nitrobenzoate. These magnetic moment data are very close to the spin-only values for the respective ions calculated from equation $\mu_{eff}=[4S(S+1)]^{1/2}$ in the absence of the magnetic interaction for present spin-system. The magnetic moment values calculated at room temperature for Co(II), Ni(II) and Cu(II) ions are equal to 3.88, 2.83 and 1.73 μ_B, respectively. For Co(II), Ni(II) and Cu(II) ions the magnetic moment values may be different, than the spin-only worth. In the case of Co(II) compound they are higher than the spin-only value. This difference between measured and calculated data results from a spin-orbital coupling [33]. For Ni(II) and Cu(II) complexes these values are lower. This is due to fact that the vectors L and S are aligned by the strong field of the heavy atom in opposite directions, and this diminishes the resultant magnetic moment. The experimental data suggest that compounds of Co(II) and Ni(II) seem high-spin complexes with probably weak ligand field [34].

The magnetic susceptibility values of 4-chloro-2-nitrobenzoate of Cu(II) increase with rising temperatures suggesting a weak antiferromagnetic interaction (Fig. 3). The magnetic moment values experimentally determined change from 0.27 μ_B (at 76 K) to 1.44 μ_B (at 303 K). These values are lower than the d^9 spin-only magnetic moment μ_{eff}=1.73 μ_B. Such dependence is a typical behaviour for copper dimer (Table 4, Fig. 4) [34–37]. The magnetic moment values of the Cu(II) complex decrease from 1.44 μ_B at 303 K to 0.27 μ_B at 76 K, as a consequence of depopulation of the excited triplet (S=1) state. It is well-known that the interaction between two S=1/2 metal atoms in a dimer leads to two molecular states: a spin singlet (S=0), and a triplet (S=1) separated by 2J. The interaction will be antiferromagnetic (J<0) if S=0 is the ground state; on the contrary if S=1, the interaction will be ferromagnetic (J>0) [38–42].

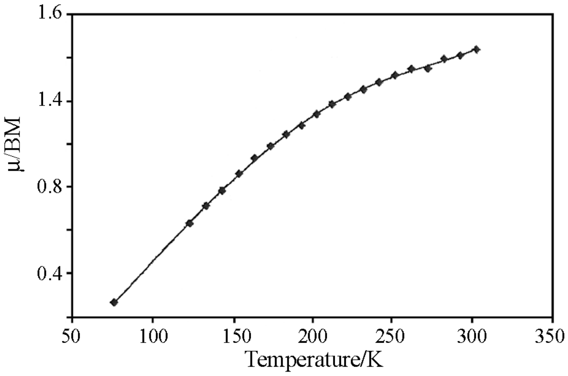

Fig. 4 Relationship between magnetic moment values *vs.* temperatures for compound of Cu(II)

Conclusions

4-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II) were characterized by elemental analysis, thermal stability in air atmosphere, IR spectral data, X-ray powder analysis, solubility in water at room temperature, and magnetic properties. The obtained results indicate them to be mono- or trihydrates. Their thermal stability was studied at 293–523 K. It was found that on heating in air above 523 K they decompose explosively. When heated they dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. The solubility of the analysed compounds in water (at 293 K) is of the order of 10^{-4}–10^{-2} mol dm^{-3}. The measured values of magnetic susceptibilities for Co(II) and Ni(II) complexes obey the Curie–Weiss law, since they decrease with rising temperatures. The obtained μ_{eff} values of Co(II) and Ni(II) compounds may suggest that they are high-spin complexes with octahedral coordination, and the ligands form the weak electrostatic field in the coordination sphere of central ion. The magnetic susceptibility of 4-chloro-2-nitrobenzoate of Cu(II) increase with rising temperatures and the magnetic moments values suggest it to be dimer.

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