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Spectroscopic and magnetic investigations of some transition metal complexes with N-4-methoxyphenyl-N-4-chlorobenzoyl hydrazide as ligand

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Abstract

The preparation, spectroscopic and magnetic properties of ML₂Cl₂ (M = Cu(II), Mn(II), Ni(II)) and [ML₃]Cl₃ (M = Fe(III), Cr(III)), L = *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide are reported. In all the studied complexes the *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide acts as a neutral bidentate chelating ligand with coordination involving the carbonyl oxygen and nitrogen atom of the secondary hydrazide group. The complexes appear to have an pseudo-octahedral stereo-chemistry. ESR parameters ($g_1 = 4.432$, $g_2 = 1.991$, D = 0.096 cm⁻¹) and $\mu_{eff} = 3.55 \mu_B$ obtained for [CrL₃]Cl₃ also suggest the possibilities of magnetic dipole–dipole coupling interactions between Cr(III) ions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrazide; Metal complexes; IR spectra; ESR spectra; Magnetic moment

1. Introduction

The ligand *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide (L) (Fig. 1) has anti-inflammatory and weakly analgesic activities. Because the metal complexes of many drugs exhibit a greater biological activity than the ligands themselves [1] the ML_2Cl_2 (M = Cu(II), Mn(II), Ni(II)) and [ML_3]Cl_3 (M = Fe(III), Cr(III)) complexes were synthesized and investigated by spectroscopic and magnetic measurements for obtaining further informations about the local structure around the metal ions

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2. Experimental

The *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide is obtained by the Fischer method [2].

The ligand was characterized by NMR and GC-MS. The ¹H NMR spectrum (CDCl₃, δ ppm) of the ligand presents: (3.69 (s) 3H, OCH₃), (4.83 (s) 2H, NH₂) and (6.68–7.29 8H aromatic). The ¹³C NMR spectrum (CDCl₃, δ ppm) presents 10 signals, one corresponding to the C atom from the methoxy group (OCH₃) at 55.47; eight signals in the aromatic region (4CH: 114.6; 127.66; 128.40; 130.27 and 4C substituted ipso 129.0; 133.25; 136.0; 136.5) and a signal corresponding to the C atom from the carbonyl group, at 158.6 ppm. The *m/z* = 276 and 137 signals in the GC-MS spectrum confirm the proposed formula.

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Fig. 1. The structural formula of *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide.

The complexes were obtained by adding to a solution of appropriate metal salts $[CuCl_2 \cdot 2H_2O \ (0.17 \text{ g}, 1 \text{ mmol}), \text{MnCl}_2 \cdot 4H_2O \ (0.19 \text{ g}, 1 \text{ mmol}), \text{CoCl}_2 \cdot 6H_2O \ (0.23 \text{ g}, 1 \text{ mmol}), \text{NiCl}_2 \cdot 6H_2O \ (0.23 \text{ g}, 1 \text{ mmol}), \text{NiCl}_2 \cdot 6H_2O \ (0.23 \text{ g}, 1 \text{ mmol}), \text{FeCl}_3 \cdot 6H_2O \ (0.27 \text{ g}, 1 \text{ mmol}), \text{CrCl}_3 \cdot 6H_2O \ (0.26 \text{ g}, 1 \text{ mmol}) \text{ in hot } 50 \text{ ml MeOH the hydrazide ligand} \ (0.55 \text{ g} \ (2.2 \text{ mmol}) \text{ for M(II) complexes}, \text{ and } 0.83 \text{ g} \ (3 \text{ mmol}) \text{ for M(III) complexes} \]. The solutions were stirred for 30 min and left at room temperature for 24 h. The complexes were purified by repeated washing with acetone. The crude products were recrystallized from methanol. Some analytical data of the prepared compounds are given in Table 1.$

Electronic spectra in absorption of methanol solutions were registered with a Specord UV-VIS spectrometer. IR spectra were registered with a Specord IRA-75-ZEISS spectrometer, using the KBr pellet technique. NMR spectra of the ligand dissolved in deuterated chloroform were registered with a Varian Gemini-300 spectrometer. EPR spectra were recorded at 9.4 GHz (X band) using a standard JEOL-JES-3B equipment with a magnetic field modulation of 100 kHz. Room temperature magnetic susceptibility measurements were made on powdered samples using a Faraday type balance.

3. Results and discussion

Partial assignments of the IR absorption bands observed for the free ligand and the metal complexes are given in Table 2.

The IR spectrum of the ligand shows an absorption band centered at 1660 cm⁻¹ characteristic for the ν (C=O) stretching vibration. In the IR spectra of the complexes this band is shifted to the lower frequencies suggesting the coordination of carbonyl oxygen atom to the metal ions. The stretching vibration bands ν (NH₂) are significantly shifted in the spectra of the metal complexes indicating the involvment of the nitrogen atom of the secondary hydrazide group in the coordination.

The deformation bands $\delta(\text{NH}_2)$ (1618 cm⁻¹), $\tau(\text{NH}_2)$ (1320 cm⁻¹), $\gamma(\text{NH}_2)$ (1040–1030 cm⁻¹) and $\delta(\text{HNN})$ (1250 cm⁻¹) are shifted insignificantly in the IR spectra of the complexes because of the disappearance of hydrogen bonds between C=O and NH₂.

The amide II band centered at 1515 cm^{-1} remains approximately unchanged. The presence of this band in the spectra of complexes proves the ketonic form of the ligand.

From a consideration of the IR spectra it is clear that in these complexes *N*-4-methoxyphenyl-*N*-4chlorobenzoyl hydrazide acts as a bidentate neutral ligand through the carbonyl oxygen and nitrogen atoms of the secondary hydrazide group.

The electronic spectrum of the ligand presents two absorption bands at $\nu_1 = 47620 \text{ cm}^{-1}$ and $\nu_2 =$ 42 553 cm⁻¹, respectively and a shoulder at $\nu_3 =$ 35 087 cm⁻¹. The ν_1 band is assigned to $\pi - \pi^*$ transitions in conjugated organic systems, which is overlapped by the $\pi - \pi^*$ transition in the carbonyl group. The ν_2 band is characteristic for the $\pi - \pi^*$ transitions

 Table 1

 Analytical and physical data for the synthesized compound

Complexes	Color	Melting point (°C)	%C		%H		%N	
			Calculated	Found	Calculated	Found	Calculated	Found
CuL ₂ Cl ₂	Green	153	48.83	48.54	3.78	4.01	8.14	
MnL ₃ Cl ₂	Beige	146	49.49	49.20	3.83	4.05	8.25	7.98
NiL ₂ Cl ₂	Blue	153	49.40	49.00	3.81	4.02	8.20	7.86
FeL ₃ Cl ₃	Red	167	50.81	50.46	3.96	4.15	8.47	8.24
CrL ₃ Cl ₃	Green	162	51.01	50.89	3.95	4.17	8.50	8.32

Table 2 IR absorption bands (cm⁻¹)

	$\nu_{\rm as}({\rm NH_2})$	$\nu_{\rm s}({\rm NH_2})$	ν (CO) amide I	$\delta_{as}(NH_2)$	ν (CO) amide II	$\delta_s(NH_2)$	δ (HNN)
L	3360 3260	3200	1660	1618	1515	1030	685
CuL_2Cl_2	3260 3225	3175	1620	1585	1510	1010	670
MnL ₂ Cl ₂	3225 3020	2995	1625	1605	1512	1030	675
CoL ₂ Cl ₂	3170 3120		1630	1605	1515	1030	685
NiL ₂ Cl ₂	3195	3125	1630	1605	1513	1030	680
FeL ₃ Cl ₃	3360 3090	3030	1620	1605	1515	1030	685
CrL ₃ Cl ₃	3100 3030		1620	1605	1515	1030	685

in aromatic systems. The appearance of a shoulder at $\nu_2 = 35 \ 0.087 \text{ cm}^{-1}$ is caused by the $\pi \rightarrow n$ transitions in the carbonyl group.

The UV absorption spectra of the metal complexes are similar. The presence of different cations leads to a weak shift towards higher energies in these spectra. These modifications might be correlated with the involvement of N and O atoms from the ligand in the coordination, which causes a strengthening of C=O and in $-NH_2$ bonds involved in the charge transfer processes. UV absorption bands of synthesized compounds are presented in Table 3 and confirm the bidentate character of the ligand.

The electronic spectra in the visible region were recorded in order to obtain some informations on the coordination mode of metal cations to the hydrazide ligand.

The electronic absorption spectra of CuL_2Cl_2 in the visible region show one absorption band at 13 200 cm⁻¹ assigned to a ${}^2\text{E}_g(\text{D}) \rightarrow {}^2\text{T}_{2g}(\text{D})$ transition. The charge transfer band reaches up to $\approx 20~000 \text{ cm}^{-1}$ and the charge transfer band of the ligand overlaps it. The g = 2.134 value of the isotropic spectrum of the CuL_2Cl_2 is typical for a

Table 3 Absorption bands (cm^{-1}) in the electronic spectra of complexes (sh = shoulder)

Complexes	$\nu_1 ({\rm cm}^{-1})$	$\nu_2 ({\rm cm}^{-1})$	$\nu_3 ({\rm cm}^{-1})$
L	47620	42553	35087sh*
CuL_2Cl_2	47692	43000	36462sh
MnL ₃ Cl ₂	47634	42942	36405sh
[CrL ₃]Cl ₃	47676	42984	36442sh
NiL ₂ Cl ₂	47648	42956	36418sh
FeL ₃ Cl ₃	47692	43000	36462sh

 CuO_3N_3 chromophore [3]. The magnetic moment of $\mu_{eff} = 1.83 \ \mu_B$ at room temperature is normal for mononuclear complexes having no appreciable interaction between the metal ions.

The absorption spectrum of NiL₂Cl₂ shows the presence of three bands assigned to the following transitions in increasing order of energy: ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{2g}(F)$ at 13 500 cm⁻¹, ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{1g}(F)$ at 16 200 cm⁻¹ and ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{1g}(P)$ whose corresponding band is obscured by the charge transfer edge. The magnetic moment of NiL₂Cl₂ $\mu_{eff} =$ 3.15 μ_{B} is in the range normally observed for octahedral nickel(II) complexes [4].

The electronic spectrum of MnL_2Cl_2 in methanol solution shows a charge transfer band $Mn^{2+} \rightarrow L$ up to $\approx 16\ 000\ cm^{-1}$. The absence of appreciable absorption at lower energy than the charge transfer edge is consistent with a pseudo-octahedral environment



Fig. 2. Powder ESR spectrum of $[CrL_3]Cl_3$ complex at room temperature.

about the metal ions. All d–d transitions for an octahedral d⁵ ion are spin-forbidden and therefore any absorption bands will be extremely weak [5]. The ESR spectrum of MnL₂Cl₂ is characterized by a quasi-isotropic **g** tensor with principal values close to the spin-only value (g = 2.002). The magnetic moment $\mu_{\text{eff}} = 5.97 \mu_{\text{B}}$ confirms the high-spin form of the complex [6].

The electronic spectrum of [CrL₃]Cl₃ exhibits three absorption bands at: 17 700 cm⁻¹, assigned to the transition ${}^{4}T_{2g}(F) \leftarrow {}^{4}A_{2g}(F)$, at 23 300 cm⁻¹ and ${}^{4}T_{1g}(F) \leftarrow {}^{4}A_{2g}(F)$, at 36 400 cm¹, that forms part of the charge transfer band. Two absorption bands at $g_1 =$ 4.432 and $g_2 = 1.991$ were observed in the EPR spectra of the Cr(III) complexes at room temperature (Fig. 2). The low-field absorption could be assigned to isolated Cr(III) ions coordinated in a pseudo-octahedral geometry (mononuclear species), whereas the strong band could be associated to coupled Cr(III) ions, i.e. dimeric or polynuclear species [7, 8]. The large width of the $g_{\rm eff} = 2$ band absorption ($\Delta B_{\rm pp} =$ 470 G) indicates that the dominant coupling interaction between Cr(III) ions is of the dipole-dipole type. The value of the magnetic moment $\mu_{\text{eff}} = 3.55 \ \mu_{\text{B}}$ is lower than expected for octahedral Cr(III) ions and confirm the possibilities of interactions between the metal centers. The calculated value of zero-field splitting parameter ($D = 0.096 \text{ cm}^{-1}$) [9] suggests a small distortion from the octahedral environment of Cr(III).

The electronic spectrum of the complex $[FeL_3]Cl_3$ shows two shoulders at 26 540 cm⁻¹ and 27 530 cm⁻¹ that forms part of the charge transfer band [10]. The ESR spectrum of $[FeL_3]Cl_3$ is almost isotropic (g = 2.002) and confirms the high-spin form (S = 5/2) as ground state. The presence of a small signal at g = 4.27 suggests a little distortion of the octahedral symmetry around the metal ions [3]. The magnetic moment $\mu_{eff} = 5.81 \ \mu_B$ is consistent with the high-spin state.

4. Conclusions

In the ML_2Cl_2 complexes the divalent metal ion is coordinated by two *N*-4-methoxyphenyl-*N*-4-chlorobenzoyl hydrazide neutral bidentate chelating ligands with chlorine atoms completing a pseudo-octhaedral structure. The [FeL₃]Cl₃ and [CrL₃]Cl₃ complexes contain three bidentate *N*-4-methoxyphenyl-*N*-4chlorobenzoyl hydrazide ligands giving a pseudooctahedral environment around the metal ions.

The UV-VIS electronic spectra, ESR spectra and magnetic moments confirm the pseudo-octahedral structure.

In the case of the $[CrL_3]Cl_3$ complex a dipole– dipole coupling interaction between Cr(III) ions is possible.

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