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Thermal, vibrational and EPR studies of Cu(II) bromide *bis*(*p*-methylaniline) and *bis*(*m*-methylaniline) complexes

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Abstract

 $[CuBr_2(pMA)_2]$ and $[CuBr_2(mMA)_2]$ complexes (pMA: *p*-methylaniline, mMA: *m*-methylaniline) have been prepared and characterized by elemental analyses, thermogravimetric analyses, magnetic moment measurements, and IR, Raman and EPR spectroscopic studies. Coordination effects on the vibrational spectra of the ligands have been investigated. The room temperature EPR spectra of the complexes and their simulated spectra are also discussed in detail. The vibrational and EPR spectral studies suggest that the coordination sphere around Cu(II) consist of a distorted tetragonal structure.

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Keywords: Copper(II) bromide; p-Methylaniline; m-Methylaniline; IR; Raman and EPR spectra

1. Introduction

Aniline and its derivatives are of great industrial importance. Hence, investigations on the structures of these compounds and related metal-complexes are very important for a better understanding of their molecular properties. A number of first row transition metal dihalides complexes with aniline and its derivatives have been previously reported [1–6]. However, there has been no complete study on the spectroscopic and magnetic properties of these metal halide compounds.

In this paper we report thermogravimetric behaviors, vibrational and EPR spectral studies of copper(II) bromide complexes with pMA $(4-C_7H_9N = para$ -methylaniline) and mMA $(3-C_7H_9N = meta$ -methylaniline). Spectral and magnetic measurements have been used to characterize each metal complex and to interpret the type of coordination around Cu(II) metal. The theoretically simulated EPR spectra of the complexes are also discussed.

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2. Experimental

The ligands (L: pMA and mMA) and CuBr₂ were used as received from Aldrich Co. without further purification. In this report, we described the identity of the products obtained from 1:2 CuBr₂/L reaction. The complex of [CuBr₂(pMA)₂] was prepared by adding pMA (2 mmol) in ethanolic solution to a solution of CuBr₂ (1 mmol) in an equal volume of the same solvent. The complex of [CuBr₂(mMA)₂] was prepared by heating CuBr₂ (1 mmol) directly with liquid mMA (2 mmol). After stirring for an hour, the precipitated complexes were collected by filtration, washed with ether and dried under reduced pressure. Single crystals of the complexes were not isolated. Composition and purity were determined by microanalysis (C, H, N and Cu) (see Table 1).

The IR spectra were recorded using KBr discs over range $4000-400 \text{ cm}^{-1}$ and using polyethylene discs over the range $500-200 \text{ cm}^{-1}$ on a Perkin–Elmer Paragon 1000 FTIR and a Mattson 2030 Galaxy FTIR spectrometer, respectively.

The Raman spectra were recorded on a Bruker RFS/100 Raman spectrometer in the range 4000–0 cm⁻¹. The samples were excited by a near IR Nd:YaG laser delivering excitation wavelength of 1064 nm. A liquid nitrogen cooled Ge detector was used.

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Compound	Color	Found (calc.) %					
		Cu	С	N	Н		
[CuBr ₂ (pMA) ₂]	Green	14.70 (14.52)	38.44 (38.42)	6.35 (6.40)	4.17 (4.15)		
[CuBr ₂ (mMA) ₂]	Dark green	14.71 (14.52)	38.43 (38.42)	6.37 (6.40)	4.19 (4.15)		

Table 1 Analytical data of the complexes

Electronic spectra in EtOH were recorded on a Perkin– Elmer Lambda 9 UV–VIS–NIR spectrometer in the range 190–1100 nm.

Thermal analyses were made on a Mettler Toledo TG50 thermobalance under N₂ flow (flow rate, 30 cm³ min⁻¹). The samples were heated in an Al₂O₃ crucible at a rate of $10 \,^{\circ}\text{C} \, \text{min}^{-1}$.

Measurements of magnetic moments at room temperature were made using the Evans method with a Sherwood Sci. magnetic balance. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.

The EPR experiments on Cu^{2+} ($^{2}\text{D}_{5/2}$) complexes have been performed at room temperature. The field-derivative EPR spectra have been registered by a conventional X-band ($\nu = 9.5-9.8$ GHz) Bruker EMX model spectrometer employing an ac magnetic modulation technique.

3. Results and discussion

3.1. Thermal study

The major features of the thermal analysis of the complexes are summarized in Table 2. Both complexes decompose in a two-stage process. The first stage corresponds to the loss of 2 mols of ligands. The DTG curve of the complex with pMA reveals two overlapping reaction steps in which the loss of two pMA occurs. One part of the two pMA is removed in the 85-210 °C range. The remaining part is completely removed in the 210-340 °C range. In the first step (50-370 °C range) of the complex with mMA, the maximum mass losses of the complex occur at 110 and 195 °C, which correspond to the loss of mMA. The second decomposition stage consists of the loss of the 1 mol of CuBr₂, leaving a very low percentage of a residue. We could not say anything whether the decomposition steps are endothermic or exothermic due to the lack of DTA data. The initial decomposition temperature of each complex reveals that the complex with pMA is more thermally stable than the complex with mMA. The difference between the stabilities of the complexes arises from the structural and electronic change between *meta* and *para* isomers. The observed weight losses for the decomposition processes in each of the complexes compare favorably with the theoretical data listed in Table 2.

3.2. UV-Vis, IR and Raman spectra

The bands (525–600 nm) in the visible region could originate either from charge transfer or d–d transitions bands [7] and are present as shoulders on the tail of a strong charge transfer band which extends across the visible region.

All the typical bands of the pMA and mMA ligands appear in the FT-IR spectra of the metal complexes. The Raman spectrum of free pMA and FT-IR spectra of $[CuBr_2(pMA)_2]$ and pMA are shown together in Fig. 1. The Raman spectrum of free mMA and FT-IR spectra of $[CuBr_2(mMA)_2]$ and mMA are given together in Fig. 2. The Raman spectra of copper complexes exhibit strong



Fig. 1. FT-Raman spectrum of (a) pMA and FT-IR spectra of (b) pMA and (c) [CuBr₂(pMA)₂].

Table 2

Thermal decomposition process of the complexes

Compound	Process	Decomp. range (°C)	DTG peaks (°C)	Weight loss (%)	
				Found	Calculated
[CuBr ₂ (pMA) ₂]	$[CuBr_2(pMA)_2] \rightarrow [CuBr_2(pMA)]$	85–210	148	21.12	24.48
	$[CuBr_2(pMA)] \rightarrow CuBr_2$	210-340	250	25.82	24.48
[CuBr ₂ (mMA) ₂]	$[CuBr_2(mMA)_2] \rightarrow CuBr_2$	50-370	110, 195	46.02	48.97



Fig. 2. FT-Raman spectrum of (a) mMA and FT-IR spectra of (b) mMA and (c) [CuBr₂(mMA)₂].

florescence, causing disappearance of some bands. The resolvable bands and their assignments are listed in Table 3. Vibrational mode assignments of free pMA and mMA are based on ab initio and DFT studies and reported in [8,9].

The bands due to the ν NH stretching vibrations are shifted to lower wavenumber (150–120 cm⁻¹) on the formation of the complexes. This would confirm that the N atom of the amine group coordinates to Cu(II) [1–3]. The shifting to the lower frequencies can be explained as a weakening of the N–H bonds resulting from the electron drainage from the nitrogen atom due to its coordination to the metal atom [4].

The NH₂ scissoring frequencies at 1621 and 1622 cm⁻¹ in the pMA and mMA spectra, respectively, are lowered 40 cm⁻¹ by coordination. The reason for this shift is the change in nitrogen orbitals and its effect on the NH₂ force constant because of the change in HNH angle [6].

Engelter et al. [2] reported an IR study of some metal(II) halide complexes with mMA and oMA (*o*-methylaniline) based on ¹⁵N-labelling study. This is an extremely useful

Table 3 Band assignments of IR and Raman spectra of the complexes

mMA		pMA		[CuBr ₂ (mMA) ₂]		[CuBr ₂ (pMA) ₂]		Assignment	
IR	Ra	IR	Ra	IR	Ra	IR	Ra		
3435 s		3416 s	3418 w	3296 s		3286 s		vNH asym	
3354 s	3353 m	3333 s	3337 w	3353 m	3220 w	3226 s		vNH sym	
3034 m	3046 s	3056 w	3054 s	3060 w	3062 w	3056 w	3053 w	vCH ring	
3015 m,sh	3012 s	3008 m	3013 s	3020 w		3006 w		vCH ring	
2919 m	2919 s	2912 m	2917 w	2920 m	2913 w	2916 m	2916 w	vCH ₃ (asym.)	
2857 w	2857 m	2859 m	2861 m	2857 w	2856 w	2857 w		2×1469 over	
1622 vs	1622 s,b	1621 vs	1617 s	1558 s	1561 vw	1562 s	1577 w,b	NH ₂ sciss	
1591 vs	1590 m	1582 m	1581 m	1592 m	1596 m	1592 s	1597 m	$\nu CC ring$	
1493 vs	1493 vw	1514 vs		1491 s	1487 w	1508 s	1513 w,sh	vCC ring	
1469 s		1441 s		1463 s	1445 m	1440 w	1455 m	βCH ₃ (asym.)	
1381 w	1378 m	1344 m	1380 m	1374 m		1347 w	1355 w	βCH ₃ (sym.)	
1314 m	1313 m	1324 m	1324 w	1312 w		1322 w		βСН	
1293 s	1293 s	1267 vs	1271 m	1254 m	1256 m	1238 w	1239 w	νCN	
				1230 vw	1232 m	1216 m	1216 w	νCN	
1170 s	1166 m		1218 m					vCCH ₃	
1077 w	1075 w	1072 w		1130 vw	1122 w	1144 w	1145 m	NH ₂ rock ^a	
1038 w		1044 m		1032 w		1041 w		γCCH_3	
996 m	996 m	983 w		1000 w	998 m			βCCC ring	
926 w	928 w	929 w,sh		920 m		934 w		βCCC ring	
870 m			844 s	878 m			877 w	yCH ring; yCCC	
775 vs	784 w	763 m		780 vs		812 vs		yCH ring; yCCC	
726 m,sh	738 s			724 m		738 m	739 w,sh	Breathing	
691 vs			645 s	693 s	692 w			γCCC ring	
655 ^b		641 ^b		1084 vs	1085 s	1094 vs	1093 m	NH ₂ wag ^a	
557 m				537 m	549 vw	537 w		βCCC ring	
	431 w		466 s	440 m		443 m		βCCC ring	
				474 w	466 m,b	487 m	480 vw,b	ν (Cu–N)	
				389 w	360 m,b	383 m	382 vw,b	v(Cu–N)	
		324 m		322 s		332 s		γCCC ring	
	294 m			306 w	305 w	297 s	296 m,b	$\beta CNH_2; \beta CH_3$	
	234 m	212 ^b		670 s	645 m,b	635 m	633 w,sh	NH ₂ twist ^a	
				237 m	245 w	244 m	251 vw,sh	ν (Cu–Br) _t	
	216 m			218 s	224 m,b	221 m	222 vw,sh	γCNH_2	
				202 m		207 m		ν (Cu–Br) _t	

Keys; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder; ν , stretch; β , in plane bend; γ , out of plane. ^a Mode has been reassigned.

^b Mode has not been observed, but has been found based on ab initio and DFT calculations [10,11].

criterion for distinguishing NH₂ vibrations from phenyl ring modes but it does not clarify the assignment of the NH₂ modes. They assigned the band around 733 cm⁻¹ to NH₂ wagging vibration of Cu(II) complexes although this vibrational mode tends to appear in the 1200–1000 cm⁻¹ region in aniline complexes, supported by –ND₂ experiments and normal coordinate analysis [3,5], similar to the methylamine and *p*-phenylendiamine complexes [10]. We, therefore, prefer to reassign the strong bands in the 1093–1084 cm⁻¹ region in the spectra of the title complexes to the NH₂ wagging mode instead of the assignment of Engelter et al. [2] as NH₂ twisting mode.

The NH₂ wagging vibration has been theoretically found based on ab initio and DFT calculations, at 641 and 655 cm⁻¹ in free pMA and mMA, respectively [8,9]. However, this mode has not been observed due to broad bands within the range 750–530 cm⁻¹ in the spectra of free mMA and pMA. This upward shift of 450–500 cm⁻¹ in NH₂ wagging mode on complex formation seems quite large but might be due to the effect of the changes in hybridazition about the nitrogen atom [3–5].

On the other hand, the NH₂ rocking and twisting modes have been also reassigned on taking into account the new assignments [3–5,8–12]. The weak IR and Raman bands at 1130 (IR)–1122 (Ra) and 1144(IR)–1145(Ra) cm⁻¹ in the spectra of [CuBr₂(mMA)₂] and [CuBr₂(pMA)₂], respectively, have been attributed to the NH₂ rocking mode. The bands in the range of 670–633 cm⁻¹ in the spectra of complexes have been ascribed to the NH₂ twisting mode.

In substituted anilines, the ν C–N stretching appears near 1270 cm⁻¹, being relatively strong compared with the nearby bands [2]. Hence, we have assigned the bands observed at 1293 and 1267 cm⁻¹ as the ν C–N stretching for the free mMA and pMA, respectively. Absorptions attributed to this vibration occur at lower frequencies in the complexes, in line with the decrease in the C=N double bond character [11].

In the low frequency region, especially below 500 cm^{-1} , it is considered that the metal–ligand vibrations occur [12,13]. Assignments of the metal–ligand vibrations, listed in Table 3, have been given carefully by considering of the internal modes of pMA and mMA and comparing with the extensive literature reports [1–19]. The 500–200 cm⁻¹ region spectra of [CuBr₂(pMA)₂] and [CuBr₂(mMA)₂] complexes are shown in Fig. 3.

In the 480–360 cm⁻¹ region, Engelter et al. [2] found two ν (Cu–N) vibrations showing ¹⁵N-sensitivity in chloroand bromo-complexes. The C_i site symmetry requires one ν (M–N) and two ν (M–X) (X: Cl, Br or I) IR active bands [2,14]. But, some vibrational couplings among Cu–N vibrations and some of the ring modes may occur [2,11]. For this reason, the spectra of Cu(II) complexes reveals two ν (Cu–N) bands in the 487–360 cm⁻¹ region. Consequently, the normal site symmetry criteria for determining the number of expected IR active bands are not strictly applied to these complexes.

The observed ν (Cu–N) values are higher in pMA complex than in those of mMA, suggesting that there is more significant distortion in [CuBr₂(pMA)₂] as is observed in the IR spectra of chloro-and bromo-complexes of Cu(II) [2,6].

The terminal Cu–Br bond antisymmetric and symmetric stretching vibrations, i.e. ν (Cu–Br)_t; were observed in 237–251 and 202–207 cm⁻¹ region, respectively. On the other hand, the stretching vibrations of the bridging Cu–Br–Cu bonds, i.e. ν (Cu–Br)_b; should appear below 200 cm⁻¹ [16]. But, we could not observe any ν (Cu–Br)_b



Fig. 3. 500–200 cm^{-1} region spectra of (a) $[CuBr_2(pMA)_2]$ and (b) $[CuBr_2(mMA)_2].$

vibrations in the Raman spectra of complexes. The possible Cu–Br (axial) interactions must be very weak, if the bridging Cu–Br–Cu bonds exist [17–19].

Singh et al. [17] reported an X-ray study of [CuBr₂(2methylpyridine)₂]. The coordination type of CuBr₂N₂ chromophore was a distorted tetragonal pyramid with bromine and nitrogen atoms in the basal plane and the bridging bromine atom from another molecule occupying the fifth coordination site. The bond between the bridged bromide and copper was considerably longer than other two terminal Cu-Br bonds. The similar results were also observed in several Cu(II) complexes [17-21]. Hence, the appearance of the ν (Cu–Br)_t vibrations indicates tetragonal structure instead of a polymeric octahedral structure with exclusively bridging bromides for the title complexes. The difference between this tetragonal type of complex and the almost regular octahedral structures is simply a matter of distortion along the z-axis. By suitably elongating the bonds along this axis it is passed from an octahedral to a tetragonal structure with weak axial Cu-Br bonds. This distortion has been observed in most Cu(II) complexes studied so far [2,7,17-21]. It is also related that the d⁹ nonbonding configuration of the Cu atom is expected to give rise to tetragonal arrangement of the ligands [20]. We, therefore, propose molecular structure of [CuBr₂(mMA)₂] and [CuBr₂(pMA)₂] complexes as shown in Fig. 4. The coordination around Cu(II) ion consists of four bonds in a square coplanar arrangement and two weaker bonds normal to the plane which is represented as thin dotted lines.

3.3. EPR study

The first-derivative EPR signal taken from [CuBr₂-(pMA)₂] was plotted together with the simulated ones in Fig. 5. The experimental spectrum has a form that is characteristic for a conventional powdered crystalline sample containing a paramagnetic ion with an axially symmetric g factor with $g_{\parallel} > g_{\perp}$ ($g_{\parallel} = 2.18$ and $g_{\perp} = 2.05$) [22] and without any hyperfine splitting. Namely, the local symmetry of the paramagnetic center giving this signal should be axial or tetragonal. The trend $g_{\parallel} > g_{\perp} > 2$ indicates that the unpaired electron is located mainly in the $d_{x^2-y^2}$ orbital (²B₁ as ground state) [23]. Here g_{\parallel} and g_{\perp} denote effective *g*-values when the dc field is applied, respectively, parallel (B_{\parallel}) and perpendicular (B_{\perp}) to the symmetry axis of the crystalline field around the paramagnetic center.

Although one can observe a greater g_{\perp} value than g_{\parallel} in some powdered compounds, depending on the electronic configuration of the magnetic center and symmetry type of powder crystallites, the absorption that corresponds to g_{\perp} is always more intensive than the absorption corresponds to g_{\parallel} in statistically and randomly oriented solids.

The Hamiltonian describing an axially symmetric Zeeman interaction can be written as:

$$H_{aiso} = \beta_e(g_\perp(B_x S_x + B_y S_y) + g_\parallel(B_z S_z)) \tag{1}$$



pMA : p-methylaniline mMA : m-methylaniline

Fig. 4. Proposed molecular structure of Cu(II) complexes. The thin dotted lines represent the weak interactions between Cu and Br (the coordination occurs via the N atom of the ligands pMA or mMA).

where β_e and *S* denote Bohr magneton and the electronic spin angular momentum of magnetic ion, respectively.

The EPR spectrum of [CuBr₂(pMA)₂] complex has been simulated by using Lorentzian and Gaussian lineshape functions. The best fitted EPR spectrum to the experimental one



Fig. 5. X-band EPR spectrum of [CuBr₂(pMA)₂] at room temperature.

has been obtained by using Lorentzian lineshape function as seen in Fig. 5.

A statistically and randomly oriented powder system contains some crystallites in resonance at all fields, B_R varying between B_{\parallel} and B_{\perp} . For a general orientation of a single crystalline granular (or molecular unit) containing paramagnetic center, the solution of the Eq. (1) gives a resonance field as:

$$B_R = \frac{hf}{g_{eff}\beta_e} [g_\perp^2 \sin^2 \theta + g_\parallel^2 \cos^2 \theta]^{-1/2} \frac{hf}{\beta_e}$$
(2)

where θ is the angle between the magnetic field and the symmetry axis direction of any particular spin species in the powder complex. In Eq. (2) the symbol *h* and *f* represent the Plank's constant and the microwave frequency, respectively. The number of the paramagnetic centers making an angle θ with the field is proportional to $\sin \theta$. By using this weighing factor together Eq. (2), one can obtain the following expression [24] for the amplitude factor, *A*;

$$A = \frac{B_{\perp}^{2}(B_{R}^{2} + B_{\parallel}^{2})}{B_{\parallel}B_{R}^{2}[(B_{R}^{2} - B_{\perp}^{2})(B_{\parallel}^{2} - B_{\perp}^{2})]^{1/2}}$$
(3)

that is proportional to the number of paramagnetic centers giving a resonance absorption at B_R .

On the other hand, the resonance curve of any individual magnetic center has its own intrinsic line shape and width. This curve reaches its maximum at the resonance field B_R . That is regardless how far from the exact resonance field, B_R , any center can give absorption at any field even it becomes unobservable experimentally. The contribution from any center to the whole absorption line at any field depends on intrinsic line width.

By using Eq. (3) for amplitude factor, we have tried both Lorentzian and Gaussian lineshape functions for intrinsic line of randomly oriented centers to reproduce experimental spectra. The fitting parameters are as follows: $B_{\perp} = 3410$ G, $B_{\parallel} = 3197$ G, line width = 34 G. As can be seen from Fig. 5, there is a satisfying agreement between experimental and simulated spectra for Lorentzian line. The simulated spectrum gives almost all the features of the experimental one. That is the magnetic center has an axially symmetric (or at most tetragonal) crystalline local electric field.

The spectra of the complexes do not exhibit any hyperfine lines at both perpendicular and parallel parts of spectrum as reported in some Cu(II) complexes [25,26]. The reason must be the exchange-narrowing effect between Cu(II) ions. It should be noted that the paramagnetic center in our case is Cu(II) ion. Therefore, one can expect hyperfine structure in the EPR spectra due to the magnetic interactions between electronic S (= 1/2) and nuclear spins, I (= 3/2). Generally, this interaction can give rise a splitting about a few tens oersteds which is easily measurable in most of the cases.

The absence of hyperfine structure suggests the existence of exchange interactions between electronic spins of Cu(II) ions in the chain. If there is sufficiently strong exchange



Fig. 6. X-band EPR spectrum of [CuBr₂(mMA)₂] at room temperature.

interaction between neighboring electronic spins, then any spin on a particular Cu (II) ion can move around and interacts with the nuclear spins of other Cu(II) ions having statistically distributed different nuclear state. The average values of the nuclear spin of different Cu(II) ion cancel out. Thus, the observed EPR spectrum of [CuBr₂(pMA)₂] does not give any hyperfine features. In this case, the hyperfine structure is completely compressed. That is, the exchange interaction is remarkably strong. The g_{\perp} and g_{\parallel} values are related by an expression $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ and found to be less than 4, supports the exchange interaction among Cu(II) ions [25] as well.

The EPR signal taken from powdered [CuBr₂(mMA)₂] complex and simulated spectra are shown in Fig. 6. The X-band EPR spectrum shows isotropic character and does not contain any hyperfine lines. The agreement of simulated line with the experimental one supports the isotropic Zeeman interaction between magnetic ion and static field. The Hamiltonian describing the isotropic Zeeman interaction can be written as:

$$H_{iso} = g\beta_e B \cdot J \tag{4}$$

where g is Lande splitting factor, β_e Bohr magneton and J is total angular momentum of magnetic ion.

The best simulation for experimental spectrum was obtained by using the first-derivative Lorentzian lineshape function and line width of 200 G. But there is a significant discrepancy between Gaussian line and experimental data. The spectroscopic splitting parameter (g = 2.12) is completely symmetric. This situation may occur if the crystalline field is cubic (or equivalently if there is perfect tetrahedrally or octahedrally coordinated magnetic ion). We could not observe any hyperfine structure in [CuBr₂(mMA)₂]. Since the exchange interaction between Cu(II) electrons is quite strong.

The values of magnetic moment of $[CuBr_2(pMA)_2]$ and $[CuBr_2(mMA)_2]$ have been found by using Evans method as 1.68 and 1.62 μ_B , respectively. The magnetic moments of the complexes are slightly lower than the spin-only value

of a d^9 ion, showing Cu–Cu interaction [1]. The values of the effective magnetic moments are also consistent with a distorted tetragonal local environment around the Cu²⁺ ions [1,6].

In conclusion, all the spectral data reveal that the metal ions in each complex are in a distorted tetragonal environment with weak axial Cu–Br bonds. This distortion is characteristic of Cu(II) complexes and has been observed in most Cu(II) complexes studied so far [2,7,17–21]. The magnetic moments are in good agreement with theoretical estimation for 3d⁹ systems. Powder EPR spectra of Cu(II) complexes are isotropic for [CuBr₂(mMA)₂] and anisotropic for [CuBr₂(pMA)₂], suggesting an axial local symmetry with a tetragonal distortion.

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