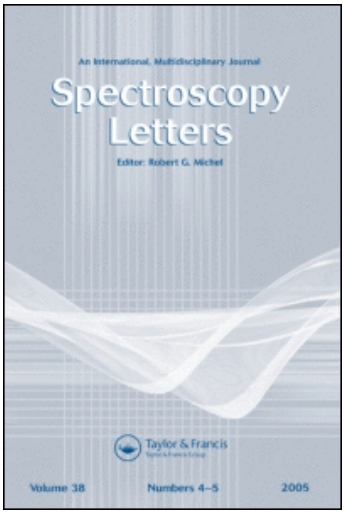

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Magnetic and Spectroscopic Studies of Metallic Halide Complexes with *N*-Methyl-1,2,4-Triazoles

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ABSTRACT Complexes of metal (II) halides with *N*-methyl-1,2,4-triazoles have been prepared, characterized, and studied by magnetism, and electronic and vibrational spectroscopies. The complex with 1:4 stoichiometry is monomeric; those of 1:1 or 1:2 stoichiometries are polymeric. It is seen from electronic studies that metal ions are trans-octahedrally coordinated and chromophores are MX_4N_2 or MX_2N_4. These structural results are in accordance with the magnitude of magnetic exchange between metallic ions. The effects of metal–ligand bond formation on the vibrational modes of the studied *N*-methyl-triazoles show the coordination mode of the ligand. In the low-frequency range, assignments of metal–nitrogen and metal-halide stretching vibrations confirm advanced structural proposals.

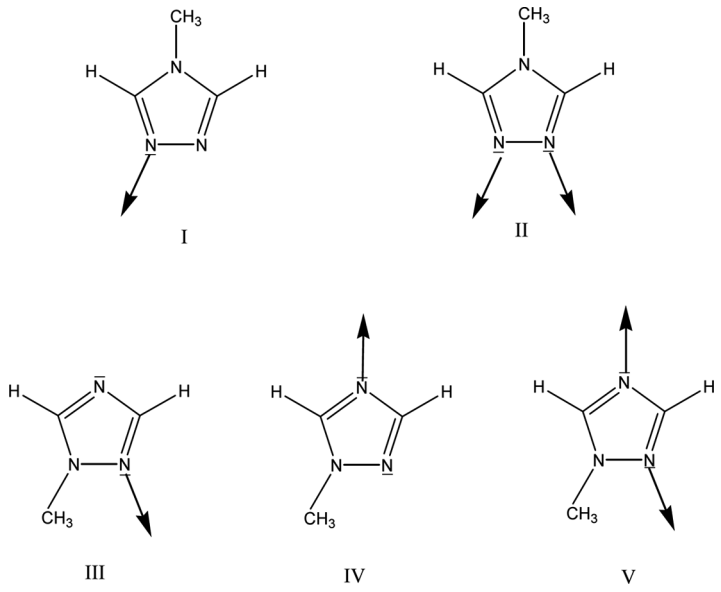
KEYWORDS metal complexes, polynuclear transition metal compounds, spectroscopic and magnetic properties, 1,2,4-triazole derivatives

INTRODUCTION

Although 1,2,4-triazoles are mainly non-natural chemicals, it is very likely that triazole–metal interactions play a major role in biological actions of triazole-containing drugs and agricultural chemicals.[1–5] To understand these interactions, further research on the geometry of triazole–metal compounds, which appear to possess a diversity of structures,[6] is of great necessity.

The current work is a part of our investigation in the field of 1,2,4-triazole complexes. Our earlier works have concerned studies of electrochemical and electronic paramagnetic resonance properties of 1,2,4-triazole cupric complexes[7] and of spectroscopic and magnetic behaviors of first transition metallic complexes of 1,2,4-triazole,[8–10] *C*-bromo-1,2,4-triazole,[11] 3,4′-bi-1,2,4-triazole,[12,13] and *N*-methyl-*C*-halogeno-1,2,4-triazole.[14]

In metallic halide complexes of 1,2,4-triazole (abbreviated as TA) with the general formula MX_2TA and MX_2TA_2 (M = Mn, Fe, Co, Ni, Cu or Zn; X = Cl or Br), TA acts as a 1,2-bridging ligand.[8–10] In order to investigate the effect of N-substitution on the complexing behavior of this ligand, we have prepared nickel and copper halide complexes of 4-methyl-1,2,4-triazole (4MeTA) and 1-methyl-1,2,4-triazole (1MeTA). Those complexes are studied



SCHEME 1 **Possible modes of coordination of 4MeTA and 1MeTA.**

by magnetism, and electronic and vibrational spectroscopies. Different modes of coordination are possible as shown in Scheme 1.

Related to some literature data, 1,2-bridges[15–17] or N_1-monodentate coordination[18–21] have been found for 4-substituted-triazoles. 1-substituted-triazoles are coordinated to metal ions as 2,4-bridging[22] or N_4-monodentate ligands.[22–25]

METERIALS AND METHODS

Starting Materials

1,2,4-Triazole (purchased from Fluka, Switzerland), metallic halides (purchased from Fluka or Riedel-de-Haen, Deutschland), and solvents (purchased from Riedel-de-Haen) were of pure quality and used without any further purification.

4MeTA was prepared as described previously[26] by desulfuration of 4-methyl-3-mercapto-1,2,4-triazole, which was synthesized by cyclization of 1-formyl-4-methyl-thiosemicarbazide, obtained from methyl-thioisocyanate and hydrazine hydrate.

1MeTA was synthesized, according to a technique reported by Bernardini et al.,[27] by direct alkylation of 1,2,4-triazole with methyl iodide in basic medium.

Synthesis of Complexes

The complexes were synthesized by adding an ethanolic solution (or an acidified ethanolic solution: acid concentration = 2 M for 1:1 complexes or 0.2 M for 1:2 and 1:4 complexes) of metallic halide ($NiCl_2 \cdot 6H_2O$, $NiBr_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CuBr_2$) to the same solution of the ligand in 1:1 or 1:2 molar ratio. An excess of the ligand has been used to elaborate $[CuX_2(4MeTA)_2] \cdot H_2O$ (X = Cl, Br) and $NiCl_2(1MeTA)_4$. The prepared complexes were filtred, washed with ethanol and ether, and then dried *in vacuo*. Their deuterated forms were elaborated by dissolving the ligand in D_2O and heating at 80°C during 24 to 48 h. They were manipulated in an isolated box and kept under vaccum in a desiccator.

Physicochemical Measurements

Elemental analyses were carried out for chloride complexes at the Lyon CNRS analytical center. The colors and analytical results for the complexes are given in Table 1. The stoichiometry of the bromides is confirmed by comparing their vibrational spectra with those of chloride analogues. To determine number of water molecules, thermogravimetric analysis curves were recorded with a Setaram thermobalance. Electronic spectra (2000–200 nm) were studied with a Perkin-Elmer model 330 recording spectrophotometer using a diffuse reflectance accessory and magnesium oxide as reference.

A classical Faraday balance with a temperature-variable accessory was used to obtain magnetic measurements from room temperature to liquid helium temperature. The field strength used was between 1500 and 13,550 G. To obtain paramagnetic

TABLE 1 Complexes of 4MeTA and 1MeTA: Elemental Analyses and Colors

Complex	C*	H*	N*	Cl*	M*	Color
$CuCl_2$(4MeTA)	16,43(16,55)	2,16(2,30)	—	32,93(32,64)	29,46(29,21)	Light blue
$NiCl_2$(1MeTA)	16,96(16,92)	2,53(2,35)	19,34(19,74)	32,87(33,38)	26,99(27,60)	Light blue
$CuCl_2$(1MeTA)	16,86(16,55)	2,30(2,30)	19,20(19,31)	31,98(32,64)	29,64(29,21)	Green
$[CuCl_2(4MeTA)_2]3H_2O$	20,41(20,30)	4,49(4,51)	24,02(23,69)	19,85(20,03)	17,56(17,92)	Green
$CuCl_2(1MeTA)_2$	23,69(23,96)	3,14(3,33)	28,17(27,95)	23,93(23,62)	21,35(21,14)	Green
$NiCl_2(1MeTA)_4$	31,07(31,18)	4,46(4,33)	35,88(36,39)	15,63(15,38)	12,42(12,72)	Green

*Found (calculated).

susceptibilities (χ_p), molar susceptibilities were corrected for diamagnetism of constituent atoms using Pascal's constants (χ_d, in 10^{-6}cgsu $\cdot$ mol^{-1})[28] and for temperature-independent paramagnetism (χ_{tip}, in 10^{-6} cgsu $\cdot$ mol^{-1}) calculated with the following relations[29]:

$$8N\mu_{B^2}/10\,D_q \quad \text{for} \quad A_2 \text{ ground terms}$$

$$4N\mu_{B^2}/10\,D_q \quad \text{for} \quad E \text{ ground terms.}$$

The D_q values were taken from ligand-field spectra. Effective magnetic moments were obtained using the relation as bellow[30]:

$$\mu_e = (8\chi_p T)^{1/2}.$$

Infrared spectra of samples as pressed disks in KCl, KBr, or polyethylene were obtained using Perkin-Elmer model 577 (4000–200 cm^{-1}) and Brucker FT I.F.S. (450–20 cm^{-1}) 113 V spectrophotometers. Raman spectra of the powdered solid compounds were recorded on a Dilor RT 30 using argon or krypton laser excitations. A rotating cell was used for the complexes, which decompose under the laser beam.

RESULTS AND DISCUSSION

Ligand-Field Spectra

The assignments of $\pi - \pi^*$, charge transfer, d-d transitions, $2\nu_{CH}$ overtones, and the calculated ligand-field parameters are given respectively in Table 2 and Table 3.

The UV bands at 49,505 and 50,760 cm^{-1} in the spectra of 4MeTA and 1MeTA bases respectively are due to a $\pi - \pi^*$ transition of the aromatic system. In the spectra of the complexes, this $\pi - \pi^*$ transition corresponds with the highest energy band. Its wavenumber decreases by complexation like in the case of other 1,2,4-triazoles complexes.[8,13,14]

Bands observed between 6200 and 5950 cm^{-1} are due to $2\nu_{CH}$ overtones. The charge transfer X $\rightarrow$ M

TABLE 2 Assignments of $2\nu_{CH}$ overtones, $\pi \rightarrow \pi^*$, Charge Transfer, and d–d Transitions (cm^{-1})

Complex	Assignments (*)							
	2νCH	$^2Eg \rightarrow {}^2T2g$				X $\rightarrow$ M	M $\rightarrow$ N	$\pi \rightarrow \pi^*$
$CuCl_2$(4MeTA)	—	7250	12300			28550	35350	43850
$CuBr_2$(4MeTA)	—	(9500)	13350			20900	30500	42900
$[CuCl_2(4MeTA)2]3H_2O$	—	9950	14850			—	35350	42000
$[CuBr_2(4MeTA)2]xH_2O$	—	10000	14550			—	26800	38750
	2νCH	$^3A2g \rightarrow {}^3T2g$	$^3A2g \rightarrow {}^1Eg(D)$	$^3A2g \rightarrow {}^3T1g(F)$	$^3A2g \rightarrow {}^3T1g(P)$	X $\rightarrow$ M	M $\rightarrow$ N	$\pi \rightarrow \pi^*$
$NiCl_2$(1MeTA)	6200	8500	(13350)	14750	25450	—	(35900)	42000
$NiBr_2$(1MeTA)	—	8400	—	14600	25250	—	(34950)	42350
$NiCl_2$(1MeTA)4	6100	8200	10450 (13350)	(14100)	16100 26100	26450	34150	40300
	2νCH	$^2Eg \rightarrow {}^2T2g$				X $\rightarrow$ M	M $\rightarrow$ N	$\pi \rightarrow \pi^*$
$CuCl_2$(1MeTA)	6150	(10100)	13600			22850	(30500)	(35700)
$CuBr_2$(1MeTA)	6200	(11100)	14100			20600	30950	40000
$CuCl_2$(1MeTA)2	6150	10200	13850			25900	30300	(38300)
$CuBr_2$(1MeTA)2	5950; 6100	(9550)	13550			—	33350	43500

*Shoulders are given in parentheses.

TABLE 3 Calculated Ligand-Field Parameters

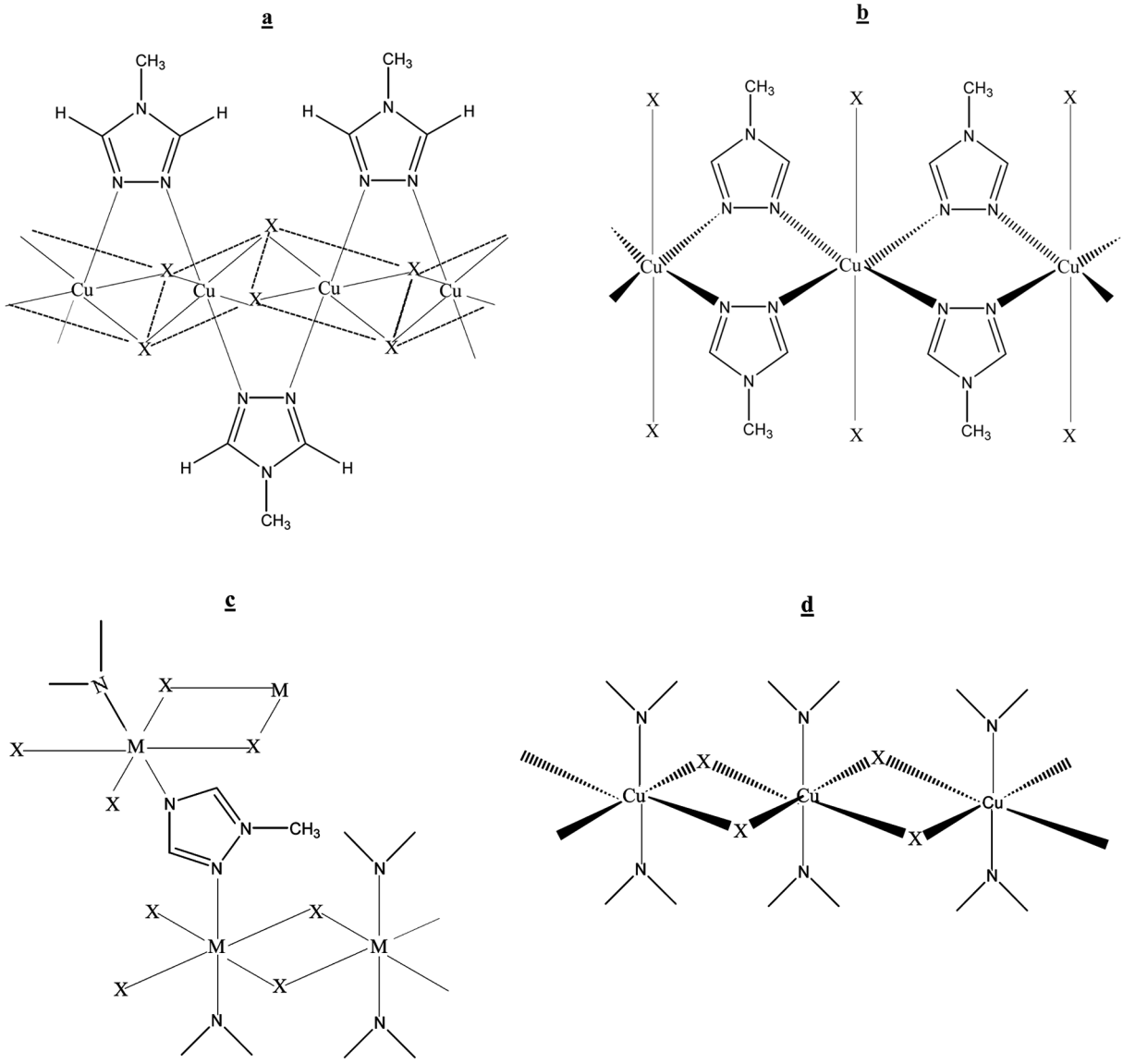
Complex	*Dq* (cm^{-1})	B (cm^{-1})	β^*
$CuCl_2$(4MeTA)	1230		
$CuBr_2$(4MeTA)	1335		
[$CuCl_2$(4MeTA)2]3H_2O	1485		
[$CuBr_2$(4MeTA)2] · H_2O	1455		
$NiCl_2$(1MeTA)	850	980	0.94
$NiBr_2$(1MeTA)	830	995	0.96
$NiCl_2$(1MeTA)4	910	935	0.90
$CuCl_2$(1MeTA)	1360		
$CuBr_2$(1MeTA)	1410		
$CuCl_2$(1MeTA)2	1385		
$CuBr_2$(1MeTA)2	1355		

$^*\beta = B/B_0$; B_0 (Ni^{2+}) = 1041 cm^{-1}.

and $M \rightarrow N$ transition energies are weaker for [CuX_2(4MeTA)$_2$]·H_2O and $NiCl_2$(1MeTA)$_4$ than for CuX_2(1MeTA)$_2$ and all 1:1 complexes with respect to the same ligand and to the same metallic salt. Indeed, a relationship seems to exist between the electronic transfer and the nature of the chromophore.[8]

Number, shapes, and positions of the d-d bands located in the near-infrared, visible, and near-ultraviolet ranges (Table 2) correspond with trans-octahedrally surrounded metallic ions.[30,31] d–d bands are assigned according to the energy level diagrams[31] and literature data.[8,11,13,14,24,32–34]

The ligand-field parameters (Table 3), obtained by the methods of calculation used previously for Ni^{II}



SCHEME 2 Proposed structural schemes of CuX_2(4MeTA) (a), MX_2(1MeTA) (b), [CuX_2(4MeTA)$_2$]·H_2O (c), CuX_2(1MeTA)$_2$ (d).

TABLE 4 **Room Temperature Effective Magnetic Moment (μ_e) Compared with Spin-Only Magnetic Moment (μ_0) and Weiss Constant (θ) Values**

Complex	μ_e (μ_B)*	μ_0(μ_B)**	θ (K)***
$CuCl_2$(4MeTA)	1.81	1.73	−16.2
$CuBr_2$(4MeTA)	1.79	1.73	
[$CuCl_2$(4MeTA)2]3H_2O	1.68	1.73	−202.5
$NiCl_2$(1MeTA)	3.14	2.83	12.3
$NiBr_2$(1MeTA)	3.20	2.83	−2.2
$CuCl_2$(1MeTA)	1.70	1.73	−46.5
$CuBr_2$(1MeTA)	1.46	1.73	
$CuCl_2$(1MeTA)2	1.89	1.73	−5.0
$CuCl_2$(1MeTA)2	1.70	1.73	

*μ_B: Bohr magneton.
**μ_0: Spin-only magnetic moment $= 2\sqrt{S(S+1)}$.
***θ calculated from $\chi_p^{-1} = f(T)$ curve.

and Cu^{II} complexes,[8] are in accordance with the proposed geometry. Their values suggest that the chromophore is MX_4N_2 for all 1:1 complexes. Consequently, halides and triazoles are bridging metallic ions respectively in the equatorial plane and in the apical positions. For $CuX_2(1MeTA)_2$ complexes, contrary to CuX_2TA_2,[8] the chromophore is MX_4N_2giving evidence of monodentate triazoles in the axial positions of the octahedra. In the case of $CuX_2[(4MeTA)_2]\cdot H_2O$ and $NiCl_2(1MeTA)_4$ complexes, the chromophore is MX_2N_4like for MX_2TA_2 complexes.[8] The halides are terminal in the apical positions and triazoles are respectively bidentate and monodentate in the plane of the octahedra. It results from these structural proposals that all complexes are polymeric; $NiCl_2(1MeTA)_4$ is monomeric.

The structure of CuX_2(4MeTA) compounds is probably analogous to that of $CuCl_2$TA. In the crystals of this complex,[35] each copper atom has a distorted octahedral coordination group consisting of four chlorine and two nitrogen atoms; the structural unit is an infinite chain in which octahedral groups are joined by sharing edges and also linked by 1,2-bidentate {4H} 1,2,4-triazoles in the axial positions. $CuX_2[(4MeTA)_2]\cdot H_2O$ present a structural scheme probably similar to that proposed for CuX_2TA_2 (Scheme 2).[8] Molecules of H_2O are not coordinated. The steric hindrance of 4MeTA comparatively to TA gives probably bigger lattice holes in which these water molecules can take place as in the case of μ-3,4-Bi-1,2,4-triazole-di-μ-chloro cuivre(II) monohydrate complex.[12]

The band splittings found in $NiCl_2(1MeTA)_4$ spectrum are similar to those observed for other complexes containing NiX_2N_4 chromophore.[8,36,37] Tetragonal distortion parameters are calculated using literature equations.[32,38]

Thus, for NiA_4B_2 chromophore under tetragonal distortion effect, the lowest excited state ^{3}T2g is dedoubled; the splitting is equal to $35D_t/4$ where D_t stands for a measure of the tetragonal distortion magnitude. The highest energy component of this doublet is equal to $10D_q^{xy}$; D_q^{xy} is the ligand-field strength due to the ligands in the (xy) plane of the

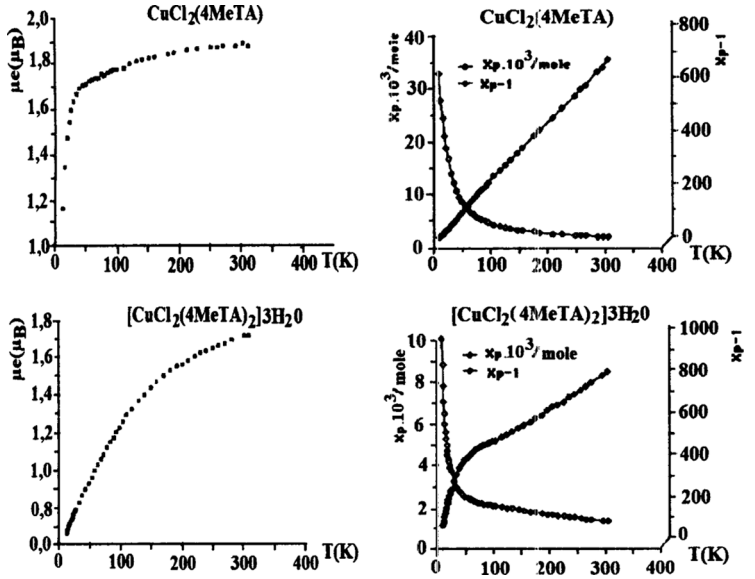


FIGURE 1 **Magnetic moment (μ_e), susceptibility (χ_p), and reciprocal susceptibility (χ_p^{-1}) versus temperature of 4MeTA complexes.**

octahedra. Ligand-field strength out of this plane is $D_q^z = D_q^{xy} - 7D_t/4$. The value of the D_s parameter is obtained from splitting of $^3T_{1g}(F)$ term: $\delta(^3T_{1g}(F)) = -6D_s^+ \ 5D_t/4$.

In the current case, the calculation gives:

$$D_q^{xy} = 1045 \text{ cm}^{-1} \quad D_t = +257 \text{ cm}^{-1}$$
$$D_q^z = 595 \text{ cm}^{-1} \quad D_s = +280 \text{ cm}^{-1}$$

By convention, D_t and D_s are positive if axial ligand-field (z axis) is weaker than the in-plane (xy) one. The splitting of the ^{3}T1g(P) lever under tetragonal distortion effect can be calculated from: $\delta(^3T_{1g}(P)) = 3D_s - 5\,D_t = 445\,\text{cm}^{-1}$. The band corresponding with $^3A2g \rightarrow {}^3T1g(P)$ transition is only broaden.

The in-plane ligand-field strength (D_q^{xy}) is greater than the axial one (D_q^z). Hence, the equatorial groups are 1MeTA while the apical ones are chlorides.

For the nickel(II) complexes studied, β values (Table 3) are indicative of less significant covalent character in metal–ligand bonds than in the case of the analogue complexes with TA.[8]

Magnetic Studies

Magnetic data are reported in Table 4. Temperature dependence of the paramagnetic susceptibility χ_p, reciprocal paramagnetic susceptibility χ_p^{-1}, and effective magnetic moment μ_e are given in Fig. 1 and Fig. 2.

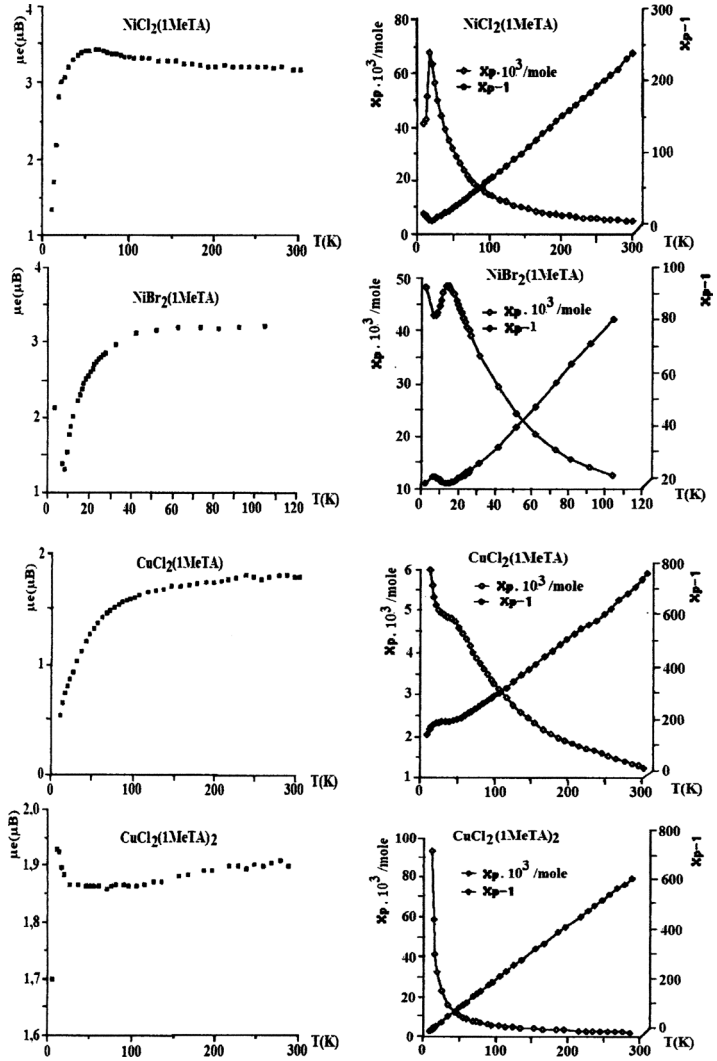


FIGURE 2 Magnetic moment (μ_e), susceptibility (χ_p), and reciprocal susceptibility (χ_p^{-1}) versus temperature of 1MeTA complexes.

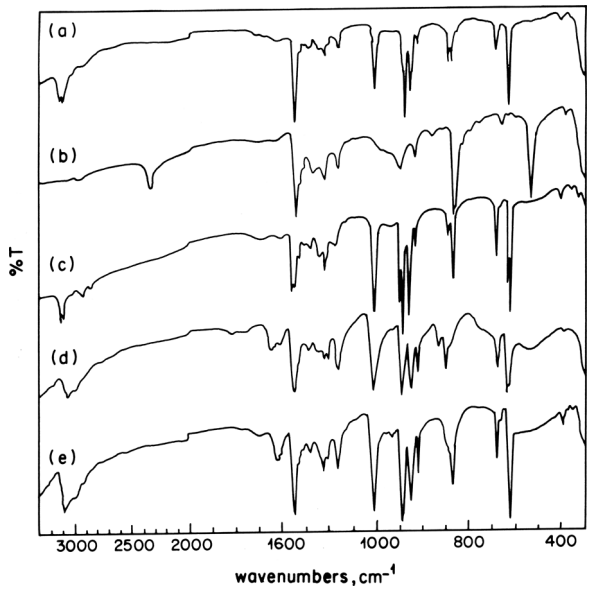


FIGURE 3 Infrared spectra in 3300–300 cm^{-1} range of $CuCl_2$-(4MeTA) (a), $CuCl_2$(4MeTA)-D_2 (b), $CuBr_2$(4MeTA) (c), [$CuCl_2$(4MeTA)$_2$]3H_2O (d), [$CuBr_2$(4MeTA)$_2$] · H_2O (e).

The room-temperature magnetic moments obtained for the studied complexes are similar to those reported for octahedral Ni^{II} and Cu^{II} compounds.[8,39,40]

The variable temperature magnetic results found for [$CuCl_2$(4MeTA)$_2$]3H_2O (Fig. 1, Table 4) are similar to those given in literature for CuX_2TA_2[8] and [Cu(tBuTA)$_2$(NCS)$_2$]1/2H_2O (tBuTA: 4-tertiobutyl-1,2,4-triazole).[21] The very strong antiferromagnetic exchange shows that more triazoles act as bridging ligands than for $CuCl_2$(4MeTA) complex and confirms that copper(II) geometry is trans. The involvement of H_2O molecules in hydrogen bonding would enhance the magnitude of the superexchange interaction. Moreover, as has been reported for CuX_2TA_2 compounds,[8] because of the steric hindrance between the organic ligands, the 4MeTA should be tilted out of the equatorial plane. This gives rise to an important d:π overlap and a facile magnetic exchange mechanism.[41,42]

Concerning 1MeTA copper(II) complexes, the exchange is significantly weaker for $CuCl_2$(1MeTA)$_2$ than for $CuCl_2$(1MeTA)according to θ-values (Table 4) and to the variation of μ_e with temperature (Fig. 2). This result is in good agreement with the electronic data: the metallic ions are linked only by chlorides in this 1:2 complex. For $CuCl_2$(1MeTA), magnetic exchange interaction between metallic ions can take place via halides and bidentate 1MeTA bridges, while in the 1:2 complex, it occurs only via halides as 1MeTA ligands are monodentate. Hence, its structure would be like to those reported for α-$CoCl_2$(pyridine)$_2$[43] and M(NCO)$_2$(1PhTA)$_2$ (1PhTA: 1-phenyl-1,2,4-triazole).[22] The broad maximum found for $CuCl_2$(1MeTA) in the susceptibility versus temperature curve (Fig. 2) is an indication of low-dimensional properties. As the bidentate 1-methyltriazoles are forced to coordinate in 2,4-fashion (Scheme 2), only a 2d-structure is possible. The struc-

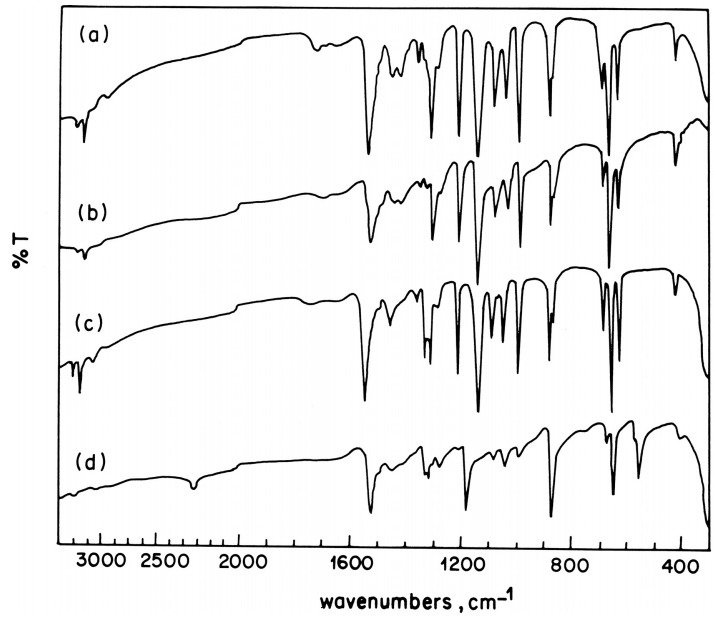


FIGURE 4 Infrared spectra in 3300–300 cm^{-1} range of $NiCl_2$(1MeTA) (a), $NiBr_2$(1MeTA) (b), $CuCl_2$(1MeTA) (c), $CuCl_2$(1MeTA)-D_2 (d).

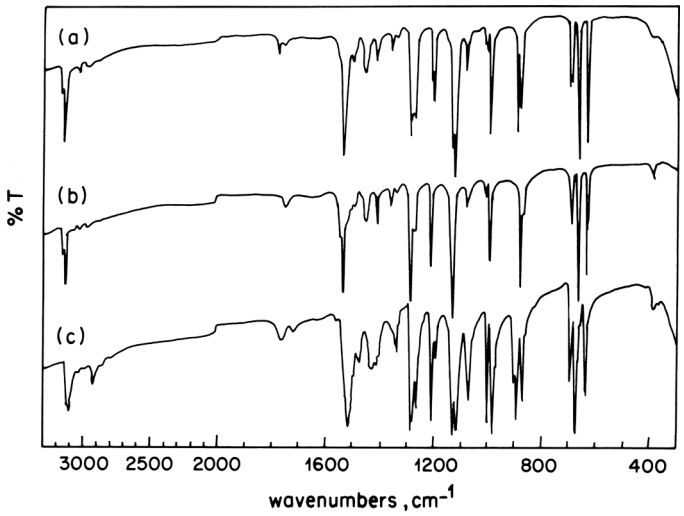


FIGURE 5 Infrared spectra in 3300–300 cm^{-1} range of $CuCl_2(1MeTA)_2$ (a), $CuBr_2(1MeTA)_2$ (b), $NiCl_2(1MeTA)_4$ (c).

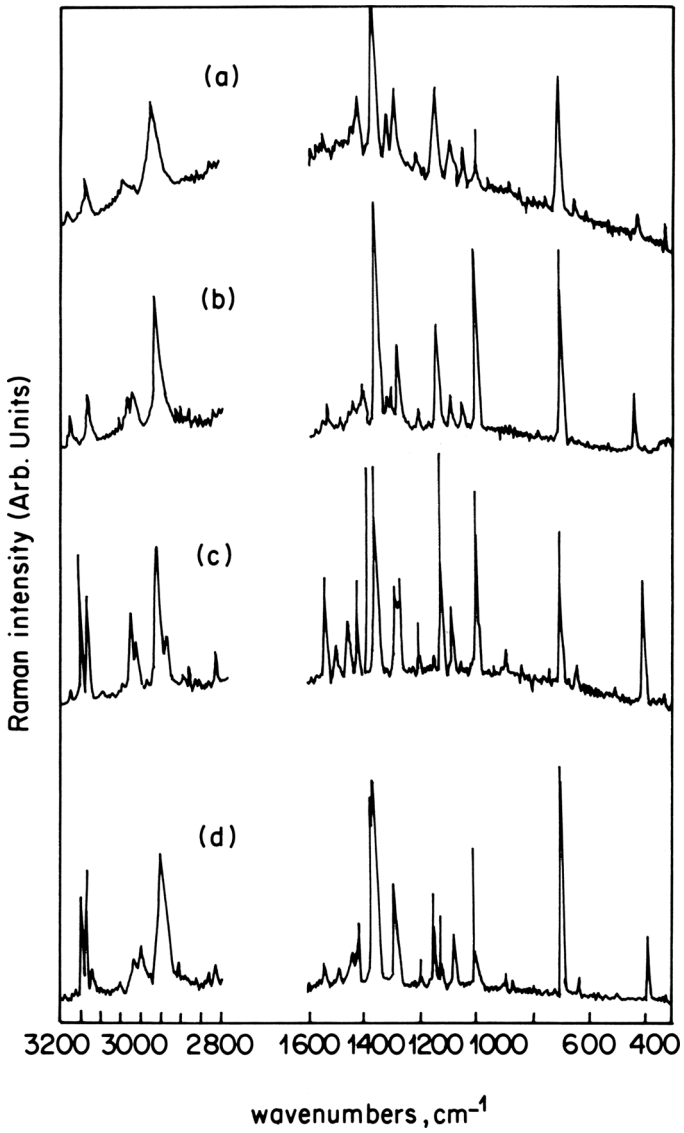


FIGURE 6 Raman spectra in 3200–2800 and 1600–300 cm^{-1} ranges of $NiCl_2(1MeTA)$ (a), $CuCl_2(1MeTA)$ (b), $CuCl_2(1MeTA)_2$ (c), $NiCl_2$-$(1MeTA)_4$ (d).

tural proposal would be similar to that of $M(NCS)_2TA_2$ in which the {1H}-TA are bridging through the 2,4-nitrogen atoms giving rise to a 2d magnetic exchange.[44,45]

The θ-values (Table 4) and μ_e versus T plots (Fig. 2) indicate that the intralayer exchange is ferromagnetic in the case of $NiCl_2$(1MeTA), while for $NiBr_2$(1MeTA), a weak antiferromagnetic interaction is found. The χ_p versus T plots for NiX_2(1MeTA) (Fig. 2) show a sharp maximum at 14 K (X=Cl) and 12 K (X=Br); this behavior is similar to that observed for NiX_2TA complexes[8] indicating probably a long-range magnetic exchange.

Vibrational Spectra

Some infrared and Raman spectra in the ligand vibration range are reproduced in Figs. 3–6. Figures 7–9 show infrared spectra of the complexes in the low-frequency range. Assignments of the ligand vibrations and those of M–N and M–X links stretching modes are given in Tables 5–8.

The vibrations of the complexes under consideration can be divided into two groups: triazole ligand and metallic skeleton. Assignments of ligand vibrations are based on deuterium isotopic effects and on comparisons with the spectra of 4MeTA[46] and 1MeTA[47] bases and with our precedent vibrational data of triazoles complexes.[9,11,13,14] In the low-frequency region, we used the concept of "X-sensitive" modes that is employed for halide metallic complexes.[48]

Previous structural studies of $[CuCl_2bTA]H_2O$[13] and $Mn_2(NCS)_4(4MeTA)_5$[15] showed that, upon complex formation, the triazoles remain quite planar. Moreover, according to our vibrational results concerning the 4MeTA base and its hydrochloride in which CH_3 group adopts a privileged geometry,[46] we admit that both 4MeTA and 1MeTA ligands in

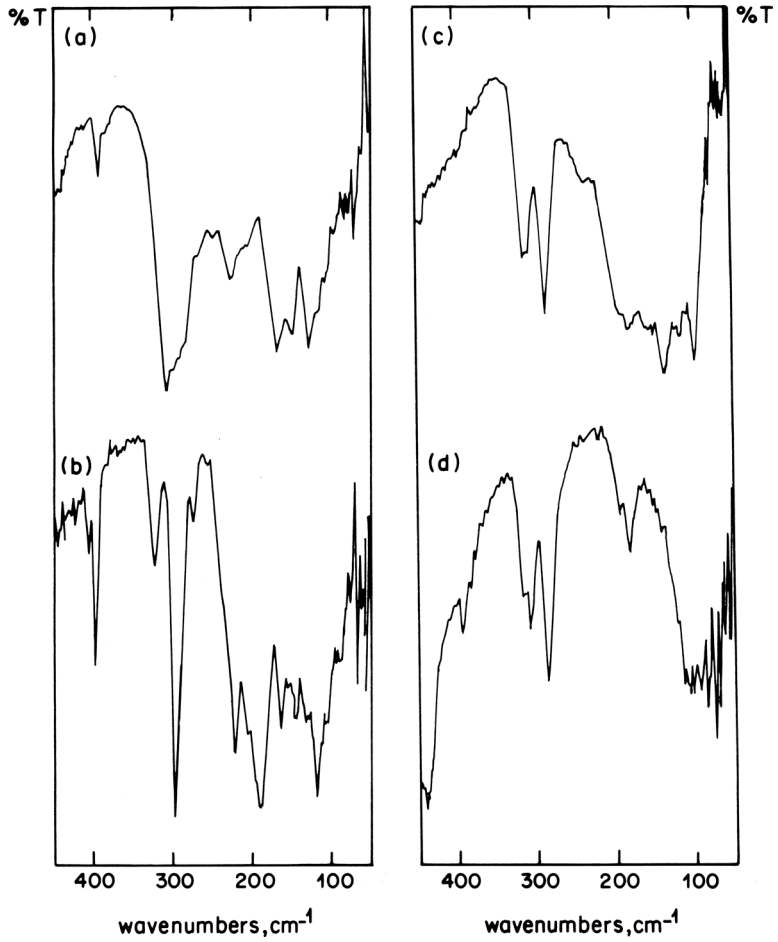


FIGURE 7 Infrared spectra in 450–50 cm^{-1} range of $CuCl_2$(4MeTA) (a), $CuBr_2$(4MeTA) (b), $[CuCl_2(4MeTA)_2]3H_2O$ (c), $[CuBr_2(4MeTA)_2]\cdot H_2O$ (d).

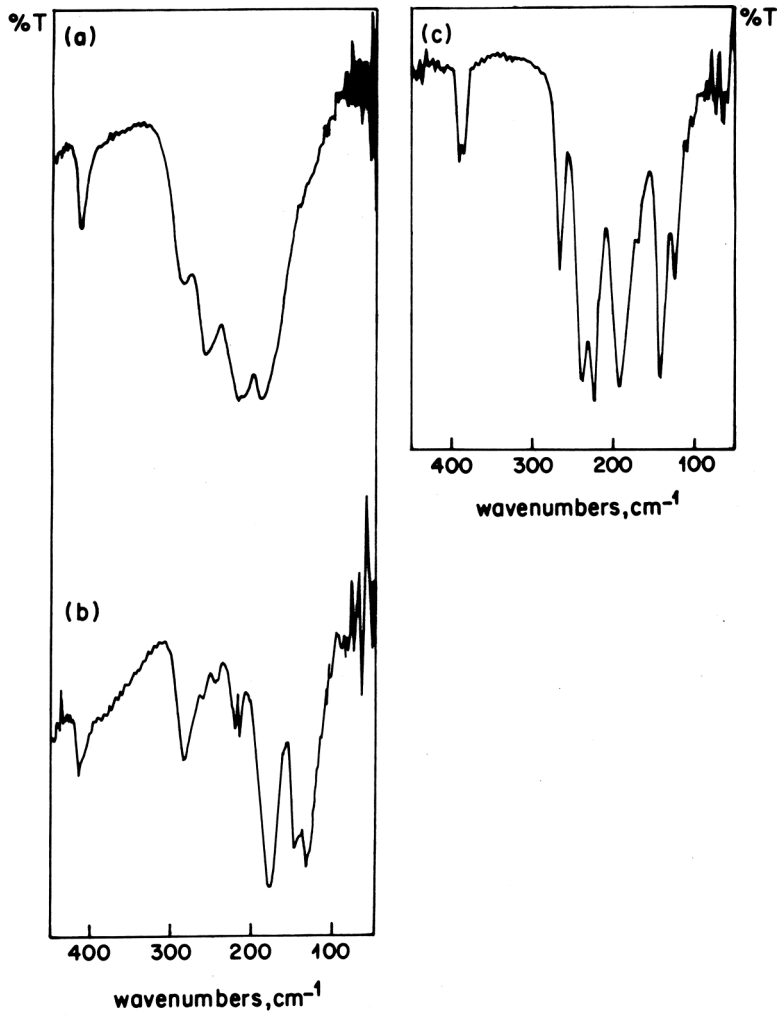


FIGURE 8 Infrared spectra in 450–50 cm^{-1} range of $NiCl_2$(1MeTA) (a), $NiBr_2$(1MeTA) (b), $NiCl_2(1MeTA)_4$ (c).

the studied complexes are planar and belong to C_s point group symmetry.

The triazole ligands have 11 atoms, and one expects 27 fundamental vibrations which fall into 18 in-plane vibrations of the A′ species and 9 out-of-plane modes of the A″ species. All these vibrations are active in both IR and Raman.

Using vibration group approximation, we have:

$$18A' = 2\nu_{CH} + 2\delta_{CH} + R_1 \text{ to } R_7 + \nu_{NCH3} + \delta_{NCH3} + \nu_s + \nu'_s + \delta_s + \delta'_s + r_{//}$$

$$9A' = 2\gamma_{CH} + \gamma_{NCH3} + R_8 + R_9 + \nu_a + \delta_a + r_\perp + t_{CH3}$$

The notations used are the same as those given previously.[46,47]

Only the vibrational results that are a useful insight into the structure of the complexes are discussed here.

Generally, apart from metal–ligand vibrations, the spectra of complexes with the same ligand are relatively similar. However, as for MX_2TA_2[9] and for metallic complexes with other organic ligands,[49–51] some band splittings are observed in the case of complexes with more than 1:1 stoichiometry (Figs. 3, 5, 6). This behavior may be due to interaction resulting from neighboring triazoles.

It was known[52,53] that infrared spectroscopy can provide useful information on the coordination mode of the triazole nucleus by focusing attention upon the triazole out-of-plane absorptions R_8 and R_9. In the current study, our attention is mainly focused to find a correlation between gaps of other cyclic vibration frequencies of the ligands upon complexation and their mode of coordination.

The results are compared with those of MX_2TA and MX_2TA_2 complexes[9] in which TA is 1,2-bicoordinating and with literature data obtained for other 1,2,4-triazole complexes in which the ligand is monodentate[22] or bidentate.[11,13,14,52] It has been

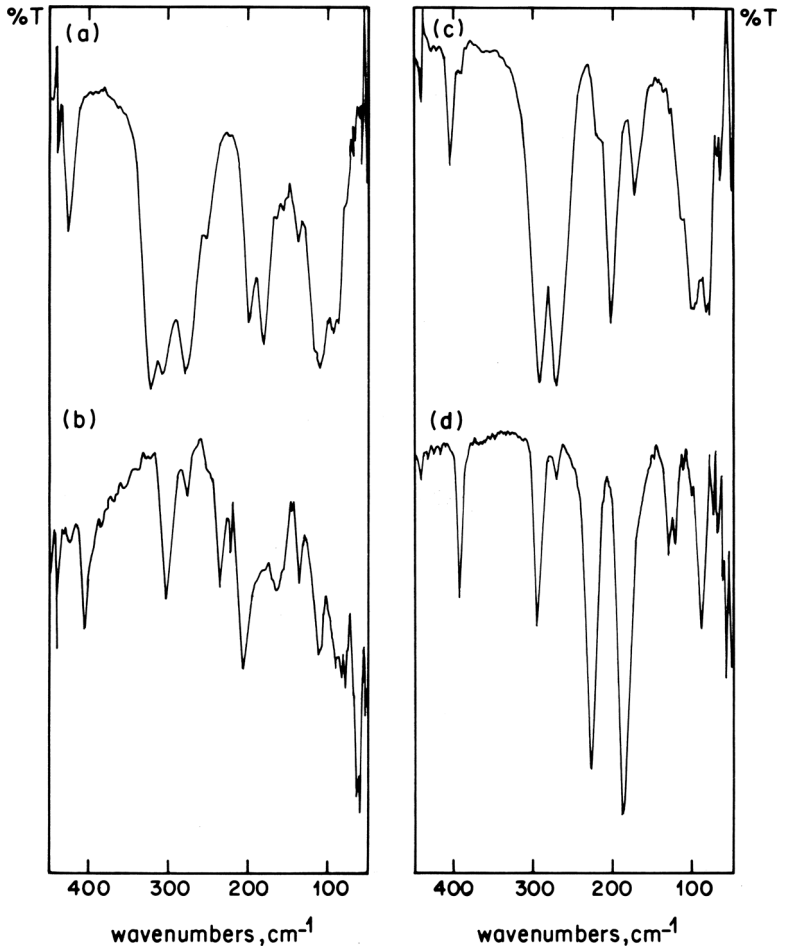


FIGURE 9 Infrared spectra in 450–50 cm^{-1} range of $CuCl_2$(1MeTA) (a), $CuBr_2$(1MeTA) (b), $CuCl_2$(1MeTA)$_2$ (c), $CuBr_2$(1MeTA)$_2$ (d).

TABLE 5 Ligand Vibrations Assignments for the 4MeTA Complexes and the Deuterated Ones

4MeTA[46]	$CuCl_2$ (4MeTA)	$CuCl_2$ (4MeTA)-D_2	$CuBr_2$ (4MeTA)	$[CuCl_2(4MeTA)_2]$ $3H_2O$	$[CuCl_2(4MeTA)_2D_4]\cdot$ D_2O	$[CuBr_2(4MeTA)_2]\cdot$ H_2O	Attribution
3110	3155	2330	3150	3120	2320	3125	νCH(CD)
3095	3125	2330	3130	3060	2320	3090	νCH(CD)
1535	1560	1540	1570	1560, (1540)	1540	1565, (1540)	R1
1411	1430	1424	1430	1430, 1420	1432	1415	R2
1360	1365	1369	1380	1365	1365	1370, (1345)	R3
1189	1215	—	1215	1220	1177	1220	R4
1211	1215	866	1215	1220	863	1220	δCH(CD)
1189	1080	830	1085	1090	840	1090	δCH(CD)
1077	1045	1097	1060	1050	1096	1055	R5
982	1020	1034	1030	1020	1035	1020	R6
966	—	960	—	930	944	915	R7
870	885	530	890	900	530	890	γCH(CD)
870	870	530	870	885	530	890	γCH(CD)
676	680	660	690	675	667	680, (670)	νNCH3
669	680	660	680	675	667	680	R8
627	625	530	620	635	535	630	R9
—	390	385	400	390	370	395, (390)	δNCH3

Note: Shoulders are given in parentheses.

TABLE 6 Ligand Vibrations Assignments for the 1MeTA Complexes and the Deuterated One

1MeTA[47]	$NiCl_2$ (1MeTA)	$NiBr_2$ (1MeTA)	$NiCl_2$ $(1MeTA)_4$	$CuCl_2$ (1MeTA)	$CuCl_2$ (1MeTA)-D_2	$CuBr_2$ (1MeTA)	$CuCl_2$ $(1MeTA)_2$	$CuBr_2$ $(1MeTA)_2$	Attribution
3130	3170	3170	3130	3180	2330	3160	3150	3140	νCH(CD)
3130	3125	3120	3110	3130	2330	3125	3130	3125	νCH(CD)
1515	1540	1535	1525, (1505)	1540	1525	1540	1535	1540	R1
1420	1425	1420	1425, 1415	1410	1420	1410	1420	1415	R2
1348	1355	1350	1345, (1340)	1350	1322	1355	1355	1365	R3
1278	1310	1305	1285	1305	1279	1300	1285	1290	R4
1215	1285	1275	1270, (1265)	1285	875	1275	1275	1275	δCH(CD)
1145	1210	1210	1215	1210	875	1215	1205	1215	δCH(CD)
1070	1140	1140	1130	1130	1182	1130	1120	1130	R5
1008	1035	1025	1000	1040	1045	1035	1005	1010	R6
960	985	985	985, 980	990	993	995	990	995	R7
880	875	870	895	875	555	895	890	880	γCH(CD)
880	875	860	870, (860)	865	555	865	880	875	γCH(CD)
680	685	680	695, (670)	685	669	685	695	695	νNCH3
680	660	660	680	650	650	665	665	670	R8
640	630	625	635, 635	625	555	635	635	635	R9
465	415	415	(390), 385, (375)	420	400	405	405	395	δNCH_3

Notes: Shoulders are given in parentheses.

seen that the magnitude of frequency shifts observed in the spectra of the complexes with respect to the free bases can be used to distinguish between the different modes of coordination of the triazole ligands under study.

These shifts are generally important and approximately similar for the 4MeTA ligand in both 1:1 and 1:2 complexes in accordance with an identical mode of coordination (bidentate via N_1,N_2) (Tables 5, 6). The same observation is given for 1MeTA ligand in NiX_2(1MeTA) and CuX_2(1MeTA) on the one hand and $CuX_2(1MeTA)_2$ and $NiCl_2(1MeTA)_4$on the other hand. Moreover, R modes frequency variations are generally weaker for $CuX_2(1MeTA)_2$ and $NiCl_2(1MeTA)_4$ complexes compared with 1:1 corresponding complexes, showing that 1MeTA is monodentate in agreement with ligand-field and magnetic results. The same behavior is noted for $SnCl_4(pyrazine)_2$ and $SnCl_4$(pyrazine) complexes studied in literature in which pyrazine is respectively monodentate and bidentate.[54]

Variations of ν_{CH} frequencies for complexes with 1:1 stoichiometry and for $CuX_2(1MeTA)_2$ compared with $[CuX_2(4MeTA)_2]\cdot H_2O$ and $NiCl_2(1MeTA)_4$ are different. This is a consequence of the fact that triazoles in these later complexes are in the equatorial

TABLE 7 Assignments of Methyl Group Fundamental Vibrations

Complex	ν_a	ν_s	$\nu_{s'}$	δ_s	δ_a	δ_s	$r_\perp$
$CuCl_2$(4MeTA)	3020	2954	2954	1495	1445	1365	1045
$CuBr_2$(4MeTA)	3020	2950	2920	1490	1450	1365	1060
$[CuCl_2(4MeTA)_2]3H_2O$	3010	2955	2955	1490 (1480)	1460	1345	1050
$[CuBr_2(4MeTA)_2]\cdot H_2O$	3020	2950	2940	1490 (1480)	1455	1345	1055
$NiCl_2$(1MeTA)	3010	2960	2925	1490	1455	1355	1075
$NiBr_2$(1MeTA)	3030	2960	2940	1490	1450	1350	1075
$CuCl_2$(1MeTA)	3035	2964	2945	1495	1450	1350	1085
$CuBr_2$(1MeTA)	3020	2944	2944	1495	1445	1355	1080
$CuCl_2(1MeTA)_2$	3010	2961	2939	1500	1455	1355	1085
$CuBr_2(1MeTA)_2$	3010	2960	2930	1500	1450	1365	1075
$NiCl_2(1MeTA)_4$	3040	2946	2930	1490	(1415) 1440	(1340) 1345	(1065) 1070

Note: Shoulder are given in parentheses.

TABLE 8 Infrared and Raman Wavenumbers (cm^{-1}) and Assignments of Metallic Skeleton Stretching Vibrations

Complex	ν_a(MN)*	ν_s(MN)*	ν_a(MX)*	ν_s(MX)*
$CuCl_2$(4MeTA)	309 vs	257 M; 250 sh	309 vs	305 s
	299 sh; 290 sh	—	285 sh	—
$CuBr_2$(4MeTA)	324 m	260 M	222 s	
	297 vs	—	204 sh;189 vs	
[$CuCl_2$(4MeTA)2]3H_2O	314 M; 307 M	292 vw	183 s	
	286 s	275 vw		
[$CuBr_2$(4MeTA)2] · H_2O	316 sh; 308 s	296 w	107 vs	
	286 vs			
$NiCl_2$(1MeTA)	287 M	246 m	261 s	230 M
			221 vs	
$NiBr_2$(1MeTA)	286 M	247 vw	181 vs	
			150 vs	
$CuCl_2$(1MeTA)	320 vs; 305 vs	237 vs	320 vs	270 m
			276 vs	237 vs
$CuBr_2$(1MeTA)	302 s	240 w	234 s	—
			206 vs	172 m
$CuCl_2$(1MeTA)2	291 vs	239 vs	291 vs	239 vs
			269 vs	
$CuBr_2$(1MeTA)2	295 M	252 vw	227 vs	187 m
			187 vs	—
$NiCl_2$(1MeTA)4	267 M	262 w	192 vs	
	239 vs	249 vw		
	224 vs			

*a, antisymmetrical; s, symmetrical; vs, very strong; s, strong; M, medium to strong; m, medium to weak; w, weak; vw, very weak; sh, shoulder.

positions of the octahedral plane; the C–H groups are probably closer to the halides giving possibility of establishment of hydrogen bonding.

In the metallic skeleton range, a mutual exclusion between infrared and Raman bands is noted for the studied complexes; it is indicative of the existence of an inversion center in the chromophore. The number of $\nu_{(MN)}$ and $\nu_{(MX)}$ modes observed is identical for complexes containing the same chromophore (Table 8). The $\nu_{(MN)}$ vibrations appear at frequencies characteristic for octahedral triazoles complexes.[10,11,13,14,52] Furthermore, $\nu_{(CuN)}$ frequency is weaker for CuX_2(1MeTA) than for CuX_2(4MeTA). This may be due to the weaker basicity of 1MeTA (pKa = 2.05) compared with that of 4MeTA (Pka = 2.64) as well as to the steric hindrance caused by the proximity of the methyl group toward one of the two sites of coordination for the triazole substituted on N_1. In the case of [CuX_2(4MeTA)$_2$] · H_2O and $NiCl_2$(1MeTA)$_4$ complexes having the MX_2N_4 chromophore, $\nu_{a(MX)}$ frequency is comparable with that of MX_2TA_2 compounds,[10] where the M–X bonds are long and terminal in the apical positions of the octahedral.

Finally, on the basis of all the precedent results, we propose the structures given in Scheme 2.

CONCLUSIONS

Electronic, magnetic, and vibrational studies of *N*-methyl-1,2,4-triazoles complexes with 1:1, 1:2, or 1:4 stoichiometries have been undertaken.

Data of electronic spectroscopy have allowed us to conclude that the geometry of the metallic ions is trans-octahedral. The chromophore is MX_4N_2 for all 1:1 complexes and for CuX_2(1MeTA)$_2$ whereas [CuX_2(4MeTA)$_2$] · H_2O and $NiCl_2$(1MeTA)$_4$ possess MX_2N_4 chromophore. Except for the 1:4 complex, which is monomeric, all studied compounds are polymeric.

The magnetic study has shown that the number of triazolic bridges is greater in [CuX_2(4MeTA)$_2$] · H_2O than for CuX_2(4MeTA). In $CuCl_2$(1MeTA)$_2$ complex, only chloride bridges exist related to the magnitude of magnetic exchange. For the corresponding 1:1 complex, 2-d magnetic properties have been observed.

The vibrational spectra of the complexes in the ligand vibrations range can be used to distinguish between different modes of coordination of the *N*-methyl-triazoles studied. Hence, frequency variations of ligand vibrations by complexation are weaker for the monodentate ligands than for the bidentate ones.

Further support of the proposed structures can be obtained from low-frequency vibration spectra. An identical number of $\nu_{(MN)}$ and $\nu_{(MX)}$ modes is observed for complexes with the same chromophore. Besides, the position of $\nu_{(MX)}$ vibration for $[CuX_2(4MeTA)_2]\cdot H_2O$ and $NiCl_2(1MeTA)_4$ complexes is compatible with a long M–X terminal bond.

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