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Coordination compounds of 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol and transition metal(II) halides. Synthesis, spectral and magnetic properties

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Abstract

The synthesis and spectroscopic and magnetic properties of a series of polynuclear metal coordination compounds are described. The compounds have the general formula $MX_2(mtpH)_2$ (with M = Mn, Fe, Co, Ni, Cu and Cd; X = Cl, Br; mtpH = 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol). The IR spectra and X-ray powder-diffraction patterns indicate the presence of two structure types within the series. On the basis of their ligand-field spectra and magnetic properties a pseudo-octahedral halide-bridged linear-chain structure is derived for most of the compounds. In this structure the metal ions are surrounded by four bridging anions and two N-coordinated, mtpH ligands. Structural exceptions are $MnBr_2(mtpH)_2$ and $CoBr_2(mtpH)_2$. These compounds have a different, possibly five-coordinated, structure in which both N and O atoms of mtpH have interactions with the metal ions and/or hydrogen bonding systems.

Introduction

Transition metals are known to interact with nucleic bases of the purine and pyrimidine types and their derivatives. These interactions are of great importance in many biochemical reactions and processes. Therefore, the binding of metal ions to these types of molecules is being studied extensively. Reviews on this matter have been published regularly [1]. Studies on the naturally occurring bases in DNA have shown, that the purine ligands frequently use the imidazole type N7 atom in coordination, but N9 may also be used [2]. With adenine a didentate bridge (coordination through N3 and N9) has also been reported for several copper(II) compounds [3, 4]. Pyrimidine bases are also known to use N3 for coordination to a variety of metal ions [5].

In addition to the naturally occurring nucleic acid bases, analogs are used with modified coordination possibilities [6]. Such modifications lead to molecules that are sterically similar to the purines. However, they may have a different number of coordinating atoms. Quite a number of aza- and deazapurines have been studied [2] of which the 8-azapurines seem to be of major interest [3].

Transition metal compounds of these purine analogs might serve to assist [4, 5] in elucidating the role played by such metal ions in their interaction with DNA and RNA. The relevance of the study of such complexes is found particularly in the field of research for antitumor agents and the environmental poisoning by metal ions.

An interesting structural modification is the shift of the purine N(1) nitrogen to the bridgehead position 5. 5-Azapurines contain the 1,2,4-triazole nucleus and have no substituents at N9 or N7. The active hydrogen is thereby eliminated from the molecule. Ligands of this type offer coordinating properties that may be compared with that of the dehydronated purines. With the dimethyl derivative: 5,7-dimethyl[1,2,4]-triazolo[1,5-*a*]pyrimidine, several transition metal compounds have already been described [6–8].

The results have shown that this ligand has a strong preference for N3 coordination. Although all three non-bridgehead nitrogen atoms are available for coordination, steric reasons probably hamper coordination at N1 and N4. [1,2,4]triazolo[1,5-*a*]-pyrimidine showed more variation in coordination modes, i.e. N1 + N3, N3 and N3 + N4 [9].

In this study we describe the coordination of metal ions to the compound 5-methyl[1,2,4]-triazolo[1,5-*a*]-pyrimidin-7-ol (henceforth abbreviated as mtpH).

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mtpH is an acidic ligand ($pK_a = 6.4$ [10]), with oxygen in the keto form, the C=O stretching absorption occurring at 1700 cm^{-1}.

With the dehydronated ligand (mtp) silver(I) and copper(II) coordination compounds have been reported [11]. To investigate the reactivity towards other metal compounds, the reaction products with first-row transition metal(II) chlorides and bromides were studied. The results including magnetic and spectroscopic characterization are presented in this paper. Despite several attempts only micro-crystalline powders could be obtained, not suited for X-ray diffraction. Therefore an extensive use of spectroscopy on the several (doped) compounds had to be made.

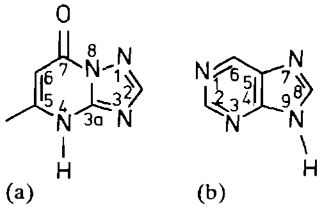
In Fig. 1 the biochemical numbering system for purines, used above, is compared with the IUPAC-recommended numbering for organic compounds. The latter numbering system is used henceforth in this paper.

Experimental

Preparations

Commercially available hydrated metal salts were used without further purification. The ligand mtpH was obtained from Janssen Chimica.

All coordination compounds were synthesized by refluxing a suspension of hydrated metal salt (2 mmol) and mtpH (4 mmol) in 30 ml of ethanol, to which a few drops of the corresponding concentrated acid were added, for 30 min (for the Cd and Cu compounds a mixture of ethanol and water was used). In most cases the suspension was directly converted into the solid metal coordination compound, without completely dissolving. The conversion was accompanied by a change of the color of the solid reactants. In the case of $CuBr_2(mtpH)_2$ instead of refluxing, a warm solution of mtpH was added to a warm solution of $CuBr_2$. And after cooling to room temperature a few ml of diethyl ether was added to precipitate the resulting copper coordination compound. The products were washed with ethanol and dried in a vacuum container at room temperature.



(a) (b)

Fig. 1. IUPAC numbering scheme of mtpH and the biochemical numbering of purine.

The cadmium compounds were doped with copper(II), cobalt(II) and manganese(II) ions by adding 2–5% of the corresponding metal salt to the suspension at the start of the reaction.

The compounds gave satisfactory analyses for metal, carbon, hydrogen and nitrogen. Table 1 lists the prepared compounds and some of their physical properties.

Physical and analytical measurements

Infrared spectra were recorded on a Perkin--Elmer 580B IR spectrophotometer in the range 4000–180 cm^{-1}. Samples were measured as KBr or CsCl pellets or as Nujol mulls between KRS-5 disks. Ligand-field spectra in the region 28000–4000 cm^{-1} were taken on a Perkin-Elmer 330 UV–Vis spectrophotometer by the use of the diffuse reflectance technique with MgO as a reference. X-band EPR powder spectra were recorded on a Varian E-3 spectrometer. Q-band EPR powder spectra were recorded on a Varian V-4500 spectrometer (University of Amsterdam). The magnetic susceptibility data were obtained in the temperature range of 4–80 K on a PAR model 150A magnetometer with the vibrating sample technique by using $CoHg(SCN)_4$ as a reference compound. X-ray powder diffraction patterns were recorded on a Philips PW-1050 powder diffractometer. The metal content of the compounds was determined by using standard EDTA titrations. C, H and N analyses were carried out by the Microanalytical Laboratory of University College, Dublin, Ireland.

Results

X-ray powder diffraction and infrared spectra

As can be inferred from Table 1, most compounds match in infrared spectra and are virtually isomorphic

TABLE 1. Composition, X-ray powder diffraction and infrared data of the coordination compounds

Number	Compound	X-ray type	IR type	$\nu(C=O)$ (cm^{-1})[a]
I	$MnCl_2(mtpH)_2$	A	a	1720
II	$MnBr_2(mtpH)_2$	B	b	1670
III	$FeCl_2(mtpH)_2$	A	a	1720
IV	$CoCl_2(mtpH)_2$	A	a	1720
V	$CoBr_2(mtpH)_2$	B	b	1670
VI	$NiCl_2(mtpH)_2$	A	a	1720
VII	$NiBr_2(mtpH)_2$	A	a	1720
VIII	$CuCl_2(mtpH)_2$	A'	a	1720
IX	$CuBr_2(mtpH)_2$	A'	a	1720
X	$CdCl_2(mtpH)_2$	A	a	1720
XI	$CdBr_2(mtpH)_2$	A	a	1720

[a] Due to interaction with overtones, the position of this band could not be measured more accurately than ±10 cm^{-1}.

according to their X-ray powder diffraction patterns. Small differences observed in the patterns can be ascribed to differences in radii of the metal and halogen ions. In the case of the copper compounds the X-ray powder patterns show somewhat larger deviations, but the infrared spectra still match well. This isomorphicity is of major importance in elucidating the structures of these compounds.

Compounds **II** and **V** feature totally different infrared spectra and powder diffraction patterns, indicating another type of structure.

In the spectrum of solid mtpH a maximum is found at 1700 cm^{-1}, which is ascribed to the C=O stretching vibration [12]. This absorption shifts to 1720 cm^{-1} in most coordination compounds, but to 1670 cm^{-1} in **II** and **V**. The upward shift is unlikely to originate from metal coordination, as no significant metal dependence was observed. Comparing it with $\nu(C=O)$ of the anionic ligand in Ag(mtp) (1670 cm^{-1}) and in $Cu(mtp)_2(NH_3)_2(H_2O)_2$ and $Cu(mtp)_2(H_2O)_4$ (1635 cm^{-1}) [11] it may be concluded that the silver–oxygen (semi)coordination and the hydrogen bonding in the copper–mtp salts cause a negative shift of $\nu(C=O)$, whereas a, most probably, 'free' C=O in the present compounds is shifted *c.* 20 cm^{-1} to a higher wavenumber. In compounds **II** and **V** the shift to 1670 cm^{-1} suggests that some kind of weak interaction of the oxygen with a metal or an acidic hydrogen must take place. These compounds also feature a very broad and strong absorption band in the region 2000–3300 cm^{-1}. A similar band is found in the infrared spectrum of solid mtpH. This absorption may indicate the presence of strong $N\text{–}H\cdots N$ type hydrogen bonding between the mtpH molecules [13].

Ligand-field spectra

The position of the very asymmetric absorption in the ligand-field spectra of the copper compounds **VIII** and **IX** (Table 2) agrees with a distorted octahedral coordination [14]. The difference in the position of the maxima results from differences in chromophores and the degree of distortion.

The ligand-field spectra of the nickel compounds indicate a distorted six coordination around the Ni(II) ions [18]. Both spectra compare well with the ligand-field spectra of the polymeric compounds $NiCl_2(py)_2$ and $NiBr_2(py)_2$ (py = pyridine) [17]. These compounds are known to have a distorted octahedral (D_{4h}) geometry [19], with the halide ions bridging between the nickel ions as shown in Fig. 2. The D_{4h} distortion causes a splitting of the (octahedral) bands. This phenomenon is most noticeable at lower energy where the band is split in two components, one weak band at about 6200 cm^{-1} ($^3B_{2g} \leftarrow {}^3B_{1g}$) and another at 8000 cm^{-1} ($^3E_g \leftarrow {}^3B_{1g}$) in the case of compounds **VI** and **VII** (Table 2).

In addition to two charge transfer bands at higher energy, the electronic spectrum of **III** features a broad symmetric absorption band at 9840 cm^{-1} and a weaker band at 6000 cm^{-1}. This could indicate a distorted octahedral geometry around the iron(II) ion [18], the distortion causing a splitting of the single band observed in the case of octahedral symmetry. Comparable observations have been made with the polymeric compound $FeCl_2(py)_2$, which is isostructural with (amongst others) $NiCl_2(py)_2$ (Table 2).

The ligand-field spectrum (Fig. 3) of compound **IV** shows an excellent agreement with the one of the compound α-$CoCl_2(py)_2$. This well-known compound has a linear-chain structure [21], similar to the already mentioned nickel pyridine compounds. However, the geometry around the cobalt(II) ion also has a slight rhombic distortion causing a further reduction of the D_{4h} symmetry to D_{2h}. The cadmium compounds, doped with cobalt(II) ions, featured very weak ligand-field spectra, thus prohibiting detailed information. However, they showed an apparent similarity with the spectra of the pure cobalt compounds. This is consistent with the fact that the infrared and powder diffraction data indicate that the cadmium compounds are isostructural with the foregoing compounds.

The electronic spectrum of **V** cannot be interpreted in terms of a regular or slightly distorted octahedral (or tetrahedral) geometry (Fig. 3). A further distortion is proposed; it may perhaps indicate a five-coordinated species instead. Similar spectra (taking into consideration band shifts caused by differences in the strengths of the ligand fields) are observed for other five-coordinated high-spin cobalt compounds [22, 18].

EPR spectra

The occurrence of three g values (Table 3) in the EPR spectrum of **VIII** reflects a rhombic symmetry around the copper ion. For the bromide compound (**IX**) the spectrum exhibits only one single broad absorption. The fact that in the case of the bromide compound no three-g-value spectrum is observed may well be due to exchange coupling between the copper ions. Similar observations have been made for halide-bridged polymeric compounds CuX_2L_2, with X = Cl,Br and L = (substituted) pyridine [23]. The latter compounds possess a similar structure as the polymeric pyridine compounds with nickel and cobalt mentioned above, the main difference being the occurrence of an asymmetric halide bridge [21, 24]. A similar distortion in **VIII** and **IX** could explain the discrepancies found in the X-ray powder patterns.

TABLE 2. Ligand field data of the compounds $MX_2(mtpH)_2$ and a few reference compounds

No.	Compound	Ligand field maxima ($\times 10^3$ cm^{-1})							Reference
III	$FeCl_2(mtpH)_2$	24.3	20.5	9.84	6.00				
	$FeCl_2(py)_2$			9.75	5.90				15
IV	$CoCl_2(mtpH)_2$	26.3		19.3^a	16.1	14.4^b	8.81	6.18	
	α-$CoCl_2(py)_2$	25.4		19.1^a	16.2	14.0^b	8.84	6.00^c	16
V	$CoBr_2(mtpH)_2$	24.0^b	22.5^b	18.4	16.3	12.8^b	8.89	5.70	
VI	$NiCl_2(mtpH)_2$	24.4	21.5^b		13.9	12.3^b	8.03	6.18	
VII	$NiBr_2(mtpH)_2$	23.3	19.8^b		13.6	11.6^b	7.96	6.14	
	$NiCl_2(py)_2$	24.1	22.2^b		13.9	12.2^b	8.40	6.00	17
	$NiBr_2(py)_2$	23.4	21.4^b	19.8^b	13.7	11.6^b	8.00	5.80	17
VIII	$CuCl_2(mtpH)_2$	26.6	14.1						
IX	$CuBr_2(mtpH)_2$	24.1	14.2						
X	$Cd(Co)Cl_2(mtpH)_2$				18.7	16.1^d			
XI	$Cd(Co)Br_2(mtpH)_2$				18.9	15.5^d			

^{a}Band consists of 3 components. ^{b}Shoulder. ^{c}Compound prepared and measured in Leiden with the use of equipment as described in 'Experimental'. ^{d}Cadmium compounds doped with Co(II) ions, spectral intensities are very weak.

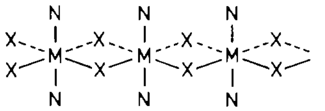


Fig. 2. Schematic structure of the polymeric pyridine compounds $MX_2(py)_2$, with X = Cl, Br [20], as proposed for compounds **I** to **XI**, with exception of **II** and **V**.

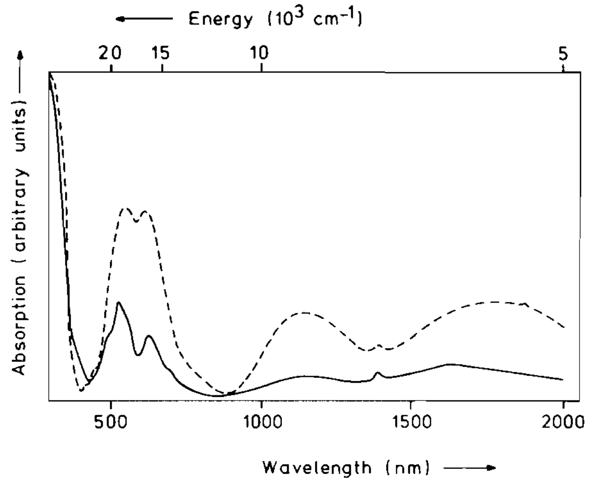


Fig. 3. The ligand-field spectra (diffuse reflectance) of $CoCl_2(mtpH)_2$ (——) and $CoBr_2(mtpH)_2$ (– – –).

The X-band EPR spectrum of **I** features only one strong broad (width ≈ 4000 G) isotropic absorption at $g = 2.02$. Similar spectra are also found for halide-bridged polymeric compounds such as $MnCl_2(py)_2$ (isostructural with α-$CoCl_2(py)_2$). Where unsymmetrical coordination is present, this type of signal is almost diagnostic of such bonding, and has been ascribed to magnetic interactions between adjacent metal ions [25, 26].

The X-band EPR spectrum of compound **III**, doped with a small amount of copper(II), features a narrow isotropic line at $g = 2.10$. The most common explanation for the observation of an isotropic Cu(II) EPR spectrum is the situation in which the complex contains grossly misaligned 'tetragonal' axes [14].

The EPR measurements of copper(II) ions, doped into the cadmium compounds (**X** and **XI**) show complicated three-g-value spectra. In both cases the spectra may indicate a distorted octahedral stereochemistry [14]. The inclusion of a small amount of iodide ions in $Cd(Cu)Cl_2(mtpH)_2$ (to compensate for the smaller radius of Cu(II) with respect to Cd(II)) resulted in better resolved EPR spectra. The Q-band EPR spectrum (Fig. 4) of this compound shows a clear resemblance with the Q-band spectrum of the chloride-bridged linear-chain compound $Cd_{0.98}Cu_{0.02}Cl_2(pz)_2$ (pz = pyrazole, $C_3H_4N_2$) [27]. The latter compound is X-ray and infrared isomorphous with $MnCl_2(pz)_2$, which is known to possess a compressed tetragonal geometry (C_2) [28]. This symmetry is reflected in the Q-band EPR spectrum of $Cd_{0.98}Cu_{0.02}Cl_2(pz)_2$ by the value of $g_3 = 2.01$, being close to the free-electron value of 2.00, indicating a d_{z^2} ground state for Cu(II) [27]. Additional evidence in favour of a (linear chain) distorted octahedral symmetry is given by the EPR spectra of the cadmium compounds doped with manganese(II) ions. At X-band frequency these compounds gave very complicated spectra differing from each other (i.e. **X** from **XI**), showing considerable splitting due to structural distortion, hyperfine and superhyperfine interactions (Fig. 5). EPR spectra of the polymeric compounds $CdX_2(py)_2$ (X = Cl or Br), doped with

TABLE 3. EPR data of the mtpH compounds

No.	Compound	Temperature (K)	EPR data		Type[e]
I	$MnCl_2(mtpH)_2$	293	$g=2.02$		X
		77	$g=2.02$		
II	$MnBr_2(mtpH)_2$	293	$g_1=3.33$, $g_2=2.01$, $g_3=1.18$		X
		77	$g_1=2.94$, $g_2=2.01$, $g_3=1.13$		
III	$Fe(Cu)Cl_2(mtpH)_2$[a]	293	$g=2.11$		X
		77	$g=2.10$		
IX	$CuCl_2(mtpH)_2$	293	$g_1=2.25$, $g_2=2.12$, $g_3=2.05$		X
		77	$g_1=2.25$, $g_2=2.10$, $g_3=2.04$		
X	$CuBr_2(mtpH)_2$	293	$g=2.13$		X
		77	$g=2.13$		
XI	$Cd(Cu)Cl_2(mtpH)_2$[a]	293	$g_1=2.28$, $g_2=2.17$, $g_3=2.03$	$A_3=91$ G[d]	X
		77	$g_1=2.27$, $g_2=2.16$, $g_3=2.02$	$A_3=73$ G	
XII	$Cd(Cu)Br_2(mtpH)_2$[a]	293	$g_1=2.25$, $g_2=2.17$, $g_3=2.03$	$A_3=69$ G	X
		77	$g_1=2.26$, $g_2=2.14$, $g_3=2.03$	$A_3=68$ G	
XI	$Cd(Cu)Cl_2(I)(mtpH)_2$[b]	293	$g_1=2.28$, $g_2=2.17$, $g_3=2.02$	$A_3=74$ G	X
		77	$g_1=2.28$, $g_2=2.16$, $g_3=2.02$	$A_3=74$ G	
		77	$g_1=2.24$, $g_2=2.20$, $g_3=2.02$	$A_3=79$ G	Q
XI	$Cd(Mn)Cl_2(mtpH)_2$[c]	293	$g_1=4.83$, $g_2=3.33$, $g_3=2.36$, $g_4=1.99$, $g_5=1.40$	$A_{Mn}=83$ G	X
		77	$g_1=5.15$, $g_2=3.58$, $g_3=2.34$, $g_4=1.98$, $g_5=1.34$	$A_{Mn}=83$ G	
XII	$Cd(Mn)Br_2(mtpH)_2$[c]	293	$g_1=6.43$, $g_2=4.21$, $g_3=2.05$	$A_{Mn}=81$ G	X
		77	$g_1=6.28$, $g_2=4.22$, $g_3=2.05$	$A_{Mn}=81$ G	

[a]Cu(II) dopes. [b]CuI_2 dope. [c]Mn(II) dopes. [d]Due to the shape of the EPR signal it was difficult to measure the exact distance. [e]X = X-band EPR spectrum, Q = Q-band EPR spectrum.

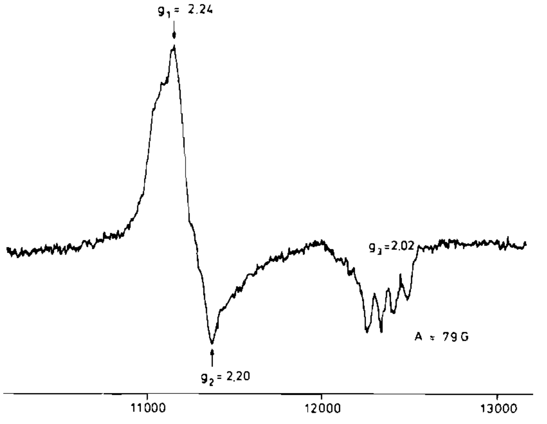


Fig. 4. The Q-band EPR spectrum of $Cd(Cu)Cl_2(I)(mtpH)_2$ at 77 K (a copper iodide dope).

manganese(II) ions, have been reported to show very similar patterns [25], indicating a corresponding structure. Both cadmium pyridine compounds are known to have structures similar to that of α-$CoCl_2(py)_2$ [29].

The EPR spectrum of the manganese bromide compound (**II**) agrees with a tetragonally distorted geometry, or a square pyramidal geometry [26, 30, 31]. The latter structure shows a better agreement with the ligand-field data of the isostructural cobalt bromide compound (*vide supra*).

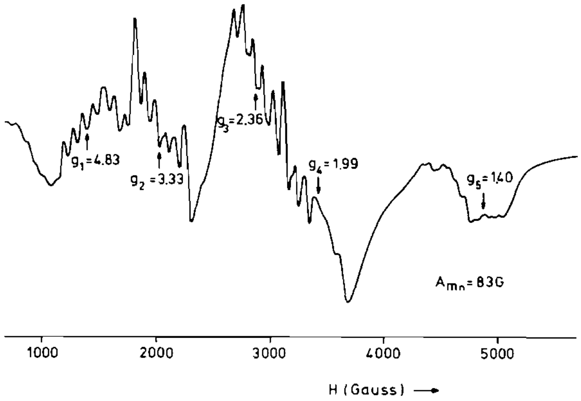


Fig. 5. The X-band EPR spectrum of $Cd(Mn)Cl_2(mtpH)_2$ at 293 K.

Magnetic susceptibility

Some magnetic susceptibility data of the mtpH compounds are summarized in Table 4. It was not possible to find a proper fit for a linear-chain model on the susceptibility data of $CuCl_2(mtpH)_2$, by using only g and J as parameters. The deviation from the

TABLE 4. Magnetic susceptibility data of mtpH compounds and a few reference compounds

No.	Compound	χ_{max} (emu mol^{-1})	T_{max} (K)	θ (K)	g	J (cm^{-1})	Note
I	$MnCl_2(mtpH)_2$	0.237	4.9	−12.7	2.02	−0.47	a, e
	$MnCl_2(py)_2$	0.263	4.0	−9	2.00	−0.49	b, e
	$MnCl_2(pz)_2$	0.168	6.5	−12	2.00	−0.63	b, e
IV	$CoCl_2(mtpH)_2$	1.05	4.9	6.7	2.85	14.7	a, e
						13.9	c
VI	$NiCl_2(mtpH)_2$			10		2.6	d
VII	$NiBr_2(mtpH)_2$			2.8		0.7	d
	$NiCl_2(py)_2$			13		3.4	d
	$NiBr_2(py)_2$			7		1.8	d

[a] g and J are fitting parameters [32]. [b] g preset at 2.00, J is a fitting parameter [32]. [c] J estimated by using Curie–Weiss law, with $\theta = J/3k$ [33]. [d] J estimated by using Curie–Weiss law, with $\theta = 8J/3k$ [34]. [e] χ_{max} = maximum in χ vs. T plot, with T_{max} = temperature at χ_{max}.

linear-chain model may be the result of interchain interactions and/or a small impurity in the sample. The value of $\theta = -9$ K is in the same region as the θ values of several other linear chloride-bridged copper complexes with pyridine derivatives ($\theta = -7$ to -14 K) [23].

It was possible to fit the magnetic susceptibility results of compound **I** as an antiferromagnetic linear chain, on the basis of the Heisenberg model and by using the scaling method of Wagner and Friedberg [35]. Table 4 displays some relevant experimental and calculated (best fit for J and g) data of compound **I** and two reference compounds, both linear chains, fitted according to the same method [32]. The data of **I** compare reasonably well with the results for the polymeric pyridine compound. Although the deviation with the pyrazole compound is more substantial, the results in all cases favour a linear-chain structure, the differences arising from differences in ligand type and (possibly) interchain distances. The best fit with the experimental χ versus T curve of compound **I** is visualized in Fig. 6.

There is a strong ferromagnetic interaction between the Fe(II) ions of compound **III** ($\theta = 22.7$ K). The μ_{eff} versus T curve exhibits a maximum at 8.5 K, where $\mu_{eff} = 20.5$ BM. The experimental values agree well with the data obtained by Long *et al.* [15] for $FeCl_2(py)_2$ in the overlapping temperature region (20–80 K) of both measurements.

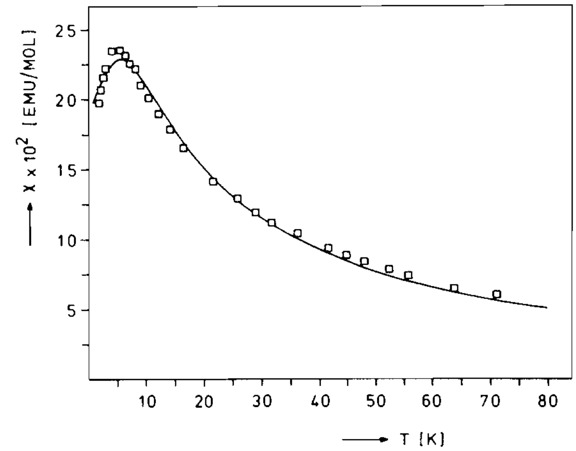


Fig. 6. χ vs. T curve of $MnCl_2(mtpH)_2$: □, experimental values; ——, best fit with $g = 2.02$ and $J = -0.47$ cm^{-1} [32].

The χ versus T curve of $CoCl_2(mtpH)_2$ exhibits a sharp maximum at $T = 4.8$ K (Table 4). A fit as a ferromagnetic chain by using the Ising model, between 12 and 80 K results in the parameters $g = 2.85$ and $J = 14.7$ cm^{-1}. These values differ significantly from fitting results of the compound α-$CoCl_2(py)_2$, by the use of the same model ($g = 5.49$ and $J = 8.1$ cm^{-1}) [33]. However, the magnetic data still point to a linear-chain system. The magnetic susceptibility results of both nickel compounds (**VI** and **VII**) point to linear-chain systems with a small ferromagnetic intrachain coupling. When comparing the estimated intrachain interaction J_i of $NiCl_2(mtpH)_2$ and $NiBr_2(mtpH)_2$, one notices that $J_i(Cl) > J_i(Br)$. This phenomenon was also observed by Witteveen *et al.* with the corresponding pyridine compounds [34] and is in contrast to many other experimental data of halide bridged linear compounds, which show a larger super-exchange via Br^- ions than via Cl^- ions [32, 36].

The isostructural compounds $MnBr_2(mtpH)_2$ and $CoBr_2(mtpH)_2$ both show an antiferromagnetic interaction between the metal ions in the region 20–80 K ($\theta = -14$ K and $\theta = -12.4$ K, respectively). When decreasing the temperature below 20 K (in the case of **V**) or below 12 K (in the case of **II**) the slope of the $1/\chi$ versus T curves suddenly steepens. This effect is quite pronounced in the case of the manganese bromide compound. The origin of this deviating behaviour might be a phase transition; however, it may also be due to the relatively strong magnetic field applied during the measurements.

Conclusions

The infrared and X-ray powder diffraction data of the mtpH compounds, clearly indicate that two structure types occur.

The results and the observed similarities in the spectral and magnetic properties of most of the mtpH compounds and known linear halide-bridged pyridine and pyrazole compounds support the suggestion that (almost) all present mtpH compounds are polymeric. In these compounds the metal ions are surrounded by six ligands, four of which are bridging anions, in a distorted octahedral symmetry. Since no significant metal dependence of the ν(C=O) vibration has been observed, only N coordination by the mtpH ligand is proposed (most likely N3 as has been found with the dehydronated ligand [11]).

In the case of MnBr$_2$(mtpH)$_2$ and CoBr$_2$(mtpH)$_2$ the results point to a different structure. The ligand-field data of CoBr$_2$(mtpH)$_2$ may suggest a five-coordinated species. The infrared spectra of these compounds indicate that possibly both N and O atoms of mtpH have interactions with the metal ions and/or acidic hydrogen atoms. A shift from N3 to N1 (and eventually O7) coordination would explain these results, leaving N1 and N4 available for the suspected N$-$H$\cdots$N type hydrogen bonding between adjacent ligands.

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