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Linear-chain Anti-ferromagnetism and Spectroscopy of Compounds CuX_2L_2, with X = Cl, Br and L = Substituted Pyridine

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A series of linear-chain systems CuX_2L_2, with X = Cl, Br and L = substituted pyridine, is prepared and investigated. I.R., far-I.R., ligand-field and ESR spectra have been recorded; furthermore, magnetic susceptibility data at low temperatures are collected in order to find out the influence of small changes in the ligand molecule on the exchange constants. The chloride and bromide compounds of each ligand appear to be isomorphous according to the I.R. spectra, although small differences in the X-ray diffraction patterns occur. The M–X and M–L frequencies, which occur in the far-infrared region, have been assigned. The ESR parameters differ only slightly for the several chloride compounds, although the g-value of the 4-Etpy compound is less anisotropic than that of the others. All bromides have nearly the same ESR spectra. The susceptibility data of the compounds have been collected over the temperature region 4.2–80.0 K. J values for the compounds are calculated using the Heisenberg model for one-dimensional systems. The data do not agree with the Ising model. All compounds behave like antiferromagnetically-coupled copper ions bridged by halogen atoms. The J values correlate with a Cu–X frequency in the far-infrared. Examination of the exchange coupling constants reveals that the J values for the bromide compounds are consistently higher than those of the corresponding chlorides. Structural data show that the magnitude of exchange is influenced by the steric effects of the different ligands. For complete understanding of the factors influencing exchange coupling in these linear-chain systems, more detailed structural data are needed.

Introduction

Magnetochemistry has grown into an active research area in inorganic chemistry. This increased importance appears to be largely due to an intense interest in weak interactions between paramagnetic centers. In highly condensed systems like metals and other three dimensional structures, the magnetic coupling usually involves great numbers of centers and gives rise to very important magnetic properties. For detailed understanding of magnetic coupling interactions in these products coordination chemistry may play an important role by supplying model systems in which the number of interacting paramagnetic centers is small. In case of paramagnetic centers built up by metal ions the systems are termed polynuclear complexes. General aims in the magnetic and structural study of polynuclear complexes are synthesis and characterization of new compounds with interesting solid-state properties, and the detailed study of complexes useful as models for understanding magnetic interactions. A second interest arises from bio-inorganic chemistry, since several metal-containing proteins have two or more centers close to each other.

The interactions studied in the present investigation involve an infinite array of paramagnetic metal ions commonly joined to diamagnetic atoms. We have investigated a group of compounds having the general formula CuX_2L_2, with X = Cl, Br and L = substituted pyridine.

To investigate the influence of small changes in the ligand molecule on the exchange constants, far-infrared, paramagnetic resonance and magnetic susceptibility measurements have been carried out on powdered samples.

Single crystal X-ray analyses of $CuCl_2(py)_2$ [1], $CuBr_2(py)_2$ [2], $CuCl_2(4\text{-Etpy})_2$ [3] and $CuCl_2(4\text{-Vipy})_2$ [4] have shown that the metal ions are surrounded by a distorted octahedron of four halogen atoms and two ligands. The octahedra share edges of halogen ions to form linear chains of metal ions, separated by the unidentate non-bridging ligands. Fig. 1 shows that the halogen bridge is asymmetric. Although the structure of $CuBr_2(py)_2$ is not completely isomorphous with the $CuCl_2(py)_2$ structure, the

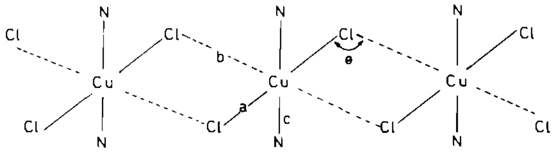

Figure 1. Illustration of the basic structural unit in compounds CuX_2L_2, with X=Cl. $a \sim 2.30$ A; $b \sim 3.10$ A; $c \sim 2.00$ A; $\theta \sim 91°$.

TABLE I. Chemical Analysis of Compounds CuX_2L_2, with X = Cl, Br and L = Substituted Pyridine

Compound	%Cu		%C		%H		%N	
	cal.	exp.	cal.	exp.	cal.	exp.	cal.	exp.
$CuCl_2(py)_2$[a]	21.7	21.5	41.0	41.2	3.42	3.47		
$CuCl_2(3\text{-Mepy})_2$[b]	19.8	20.2	44.9	43.9	4.41	4.32	8.74	8.37
$CuCl_2(4\text{-Mepy})_2$[b]	19.8	19.8	44.9	45.1	4.41	4.47	8.74	8.61
$CuCl_2(4\text{-Etpy})_2$[c]	18.2	18.6	48.2	47.9	5.16	5.17	8.03	7.83
$CuCl_2(4\text{-Vipy})_2$[d]	18.4	18.3	48.7	48.7	4.06	4.16		
$CuCl_2(4\text{-Acpy})_2$[e]	16.9	17.0	44.6	44.5	3.72	3.64		
$CuCl_2(4\text{-Mison})_2$[e]	15.5	15.5	41.1	41.4	3.43	3.64		
$CuCl_2(3,4\text{-diMepy})_2$[b]	18.2	18.8	48.2	46.9	5.21	5.06	8.03	7.74
$CuCl_2(3,5\text{-diMepy})_2$[b]	18.2	18.0	48.2	47.0	5.21	5.24	8.03	8.13
$CuCl_2(3,5\text{-diClpy})_2$	14.8	14.2	27.9	28.3	1.39	1.59	6.51	6.46
$CuBr_2(py)_2$[f]	16.7	16.6	31.4	30.9	2.62	2.63		
$CuBr_2(3\text{-Mepy})_2$[g]	15.5	15.2	35.2	34.8	3.45	3.42	6.84	6.45
$CuBr_2(4\text{-Mepy})_2$[h]	15.5	15.0	35.2	35.0	3.45	3.41	6.84	6.69
$CuBr_2(4\text{-Etpy})_2$[i]	14.5	14.5	38.4	38.2	4.11	4.34	6.40	6.28
$CuBr_2(4\text{-Vipy})_2$	14.7	14.5	38.7	38.3	3.23	3.14		
$CuBr_2(4\text{-Acpy})_2$	13.6	13.7	36.1	36.2	3.01	3.00		
$CuBr_2(4\text{-Mison})_2$	12.8	12.9	33.8	34.2	2.81	2.86		
$CuBr_2(3,4\text{-diMepy})_2$	14.5	14.6	38.4	38.1	4.15	4.29	6.40	6.22
$CuBr_2(3,5\text{-diMepy})_2$	14.5	14.4	38.4	37.7	4.15	4.18	6.40	5.95
$CuBr_2(3,5\text{-diClpy})_2$	12.2	12.2	23.1	23.3	1.16	1.16	5.39	5.34

abbreviations:
3-Mepy = 3-methylpyridine, 4-Mepy = 4-methylpyridine, 4-Etpy = 4-ethylpyridine, 4-Vipy = 4-vinylpyridine, 4-Acpy = 4-acetylpyridine, 4-Mison = 4-methylisonicotinate, 3,4-diMepy = 3,4-dimethylpyridine, 3,5-diMepy = 3,5-dimethylpyridine, 3,5-diClpy = 3,5-dichloropyridine.

[a] First prepared by Lang [12]. [b] First prepared by Frank and Rogers [13]. [c] First prepared by Burgess [14]. [d] First prepared by Agnew and Larkworthy [15]. [e] First prepared by Wong and Brewer [16]. [f] First prepared by Pfeiffer and Pimmer [17]. [g] First prepared by Lamar [18]. [h] First prepared by Allan *et al.* [19]. [i] First prepared by Lever and Larkworthy [20].

coordination around copper is similar [5]. Hatfield and coworkers [6, 7] investigated the above mentioned compounds and calculated the J values. We investigated a class of similar copper compounds in order to: a) have a larger number of comparisons, b) find out how the parameters a, b, c, θ influence the J value, c) compare and hopefully improve existing theories in describing linear-chain systems.

The magnetic susceptibility has been interpreted assuming the isotropic Heisenberg linear-chain model with the hamiltonian [8]:

$$H = -2J \sum_{i,j} S_i \cdot S_j$$

J is the interaction between nearest neighbours.

Jotham showed [9] that the anisotropic Ising simplification of the isotropic exchange Hamiltonian is substantially in error for the description of one-dimensional polymeric systems having large exchange constants. Following Jotham our J values are calculated according to the results of Bonner and Fisher [8], who extrapolated a "theoretical" susceptibility curve for the infinite Heisenberg S = ½ chain, from their results for finite Heisenberg S = ½ chains.

Compounds that could not be described with the Heisenberg model were tried to describe with the anisotropic Ising model. Fisher [10] published the closed form expressions for the anisotropic susceptibility of one-dimensional chains of S = ½ ions. Far-I.R., ESR and ligand-field spectra have been recorded to confirm the linear-chain structure of our compounds and to detect the presence of structural variations.

Experimental

Preparations

Compounds CuX_2L_2 (5 mmol) (X = Cl, Br and L = substituted pyridine) were prepared by mixing alcoholic solutions of the hydrated copper halides and ligand in a ratio slightly less than 1:2 in order to prevent the formation of the tetra-adducts (CuX_2L_4). For dehydration an excess of triethyl orthoformate was added to the solution. The immediately obtained precipitates were filtered off, washed several times with ethanol and diethyl ether, and finally dried *in vacuo* at room temperature.

Analysis

All samples were checked for purity by chemical analysis (Cu, C, H, and in most cases N) and I.R.-spectra. Analytical data are listed in Table I.

Physical Measurements

Ligand-field spectra were performed on a Beckman DK-2 ratio recording spectrometer, furnished with a reflectance attachment (35.000–4000 cm^{-1}). Infrared spectra were recorded on a Beckman Acculab 6 spectrometer as nujol mulls, sandwiched between potassium bromide windows (4.000–400 cm^{-1}). Far infrared spectra were recorded on a Beckman IR-720 Fourier spectrofotometer, in pressed polyethylene plates in the spectral range 500–20 cm^{-1}. X-ray powder diagrams were obtained with a Guinier camera using Cu–K_α radiation; the samples were mounted with vaseline.

ESR powder spectra were recorded on commercial Varian Instruments at X-band and at Q-band frequencies at room temperature.

Low-temperature magnetic susceptibility measurements were performed on a PAR-vibrating sample magnetometer, calibrated with a pure Ni sample, in the 4.2–80.0 K region. The temperatures were measured indirectly from potassium chromium alum [11]. All susceptibility measurements were carried out at a field strength of 9200 G. The molar susceptibility of all samples appeared to be field independent up to 18000 G.

Results and Discussion

General

The analytical results of the compounds are listed in Table I. A number of these compounds have been mentioned previously [12–20] and have been reanalysed to confirm purity. The colours of the chlorides are blue, those of the bromides green, except for $CuBr_2(3,5\text{-diClpy})_2$ which is yellow.

Infrared spectra of all compounds have been recorded to find out whether a difference occurs between the chloride and bromide complex of one ligand or not. In case of the 4-Etpy and the 4-Mison compounds small differences in the I.R. spectra occur; the other pairs can be considered as isomorphous.

The I.R. spectra showed that water, solvent and free ligand are absent in our compounds. X-ray powder diffraction patterns show, that the chloride and bromide compounds of the same ligand are not powder isomorphous, just as found for the pyridine compounds, although X-ray single crystal analysis shows that details around Cu(II) are similar [5]. It is further seen that in our series only two compounds exist, that are completely X-ray powder isomorphous, *i.e.* $CuCl_2(3\text{-Mepy})_2$ and $CuCl_2(3,4\text{-diMepy})_2$.

Far-infrared Spectra

Far-infrared spectra were recorded in order to confirm the linear-chain structure of the compounds. The observed absorptions in the 400–50 cm^{-1} region are listed in Table II, together with the free ligand absorptions. By comparing the spectra of the compounds with the spectra of the free ligand, by a study of the literature on stretching vibrations of $CuCl_2(py)_2$ [21–23] and comparing the spectra of the chlorides and bromides, the Cu–X and Cu–L vibrations can be assigned.

The Cu–L vibrations are mostly interpreted as Cu–N vibrations [21–23], however, one has to bear in mind that also vibrations due to ligand waggings and ligand torsions occur, the so-called wagging vibrations [24]. Very recently Rüede and Thornton [23] published some results for $CuCl_2(py)_2$, in which deuterated pyridine was used, re-assigning earlier data. These results do not completely agree with our assignment. To confirm our assignment, we prepared both the chloride and bromide compounds and their deuterated analogs and investigated their far-infrared spectra. These far-infrared data are included in Table II. Examination of this Table reveals that the highest Cu–L vibration, assigned to the Cu–L stretching vibration, shifts only 4 cm^{-1} on deuteration. According to this shift the 270 cm^{-1} band cannot be assigned to a Cu–Cl stretching. The other bands for X=Cl at 235, 205 and 196 cm^{-1} shift about 7–10 cm^{-1} on deuteration and according to Adams [24] must be due to Cu–L bending and wagging vibrations.

Theoretically the number of far-infrared vibrations for a species $CuX_2X'_2L_2$ in C_{2h} symmetry can be calculated. The results are listed in Table III, and are calculated according to the methods outlined by Cotton [25]. Examination of the Table reveals that we expect 12 bands ($3A_u$ and $9B_u$) in the far-infrared region. It is clear that the bending vibrations in which the X' atom (the halogen atom at longer distance) is involved, will occur at very low frequencies. The ligand wagging vibrations and Cu–L bending vibrations have the same symmetry, so we expect mixing of these vibrations. Furthermore it is clear that all 12 bands cannot be observed in the far-infrared region investigated here, *i.e.* above 50 cm^{-1}. Neglecting bendings involving the halogen atoms at longer distance, we expect 9 bands in the far-infrared; from these three are Cu–L wagging vibrations.

In the $CuBr_2(py)_2$ spectrum the Cu–Br and Cu–L stretching vibrations are very close to each other, giving rise to overlap and mixing of these vibrations. As expected, deuteration of the pyridine molecule did not yield strong evidence for discrimination between Cu–Br and Cu–L vibrations. We assigned the band of lowest intensity to the Cu–L stretching vibration, because in the spectrum of the chloride the Cu–L stretching band also has lower intensity than the Cu–Cl stretching band. Theoretical approximations

TABLE II. Far-infrared Data of the Compounds CuX_2L_2, with X=Cl, Br and L = Substituted Pyridine.

Compound	Cu–Cl (cm^{-1})	Cu–Br (cm^{-1})	Cu–L (cm^{-1})	Ligand Bands and Unassigned Bands (cm^{-1})	
				Free Ligand	Compound
$CuCl_2(3,5\text{-diClpy})_2$	302br 170m 92br		253m 200s 153m	390m 192m	399m 223w
$CuBr_2(3,5\text{-diClpy})_2$		247br 115m 67s	247br 190s 160m 147s	390m 192m	400m
$CuCl_2(4\text{-Vipy})_2$	303s 168s 75br		278s 250s 185s	220m	270sh
$CuBr_2(4\text{-Vipy})_2$		226br 127s 59s	247m 226br 174s	220m	292w 268w
$CuCl_2(py)_2$	293s 179s 78s		270s 235s 205m 196w		
$CuCl_2(py\text{-d5})_2$	293s 178s 78s		266s 225s 195m 186w		400s
$CuBr_2(py)_2$		254s 131s 64s[a]	267m 204s 195m		
$CuBr_2(py\text{-d5})_2$		250s 130s 64s[a]	264s 197s 186m		400s
$CuCl_2(4\text{-Mepy})_2$	294s 169s 69br[a]		284w 259s 207s	212m	
$CuBr_2(4\text{-Mepy})_2$		237s 125s 52br[a]	283w 257s 193s	212m	77w
$CuCl_2(4\text{-Etpy})_2$	289s 163s 62s		274m 249s 182s	396m 300s 152m	303s 92w
$CuBr_2(4\text{-Etpy})_2$		216br 120s 58s[a]	275m 246s 179s	396m 300s 152m	
$CuCl_2(3\text{-Mepy})_2$	293s 169s 74s[a]		265s 211m 192m	342m 219m	358m 233w
$CuBr_2(3\text{-Mepy})_2$		240s 129s 58s	270s 187s	342m 219m	358m
$CuCl_2(3,5\text{-diMepy})_2$	290br 164s 79s		284sh 247s 189w 181s	273m 205m	223w
$CuBr_2(3,5\text{-diMepy})_2$		240br 121s 65s	291s 240br 174s	273m 205m	215m
$CuCl_2(3,4\text{-diMepy})_2$	291br 164s 68s[b]		291br 255s 190s 145w	257m 183m	
$CuBr_2(3,4\text{-diMepy})_2$		244s 118s 59s[b]	294w 255m 180s 144w	257m 183m	214m
$CuCl_2(4\text{-Acpy})_2$	299s 176s 98s[a]		267m 242s	360m 220s 160s 90br	400w 240sh 170sh
$CuBr_2(4\text{-Acpy})_2$		232s 129m 82br[b]	278s 242m 166s	360m 220s 160s 90br	395m
$CuCl_2(4\text{-Mison})_2$	303s 168s 93br		266w 232br	338br 217w 216br 167m 70s	398m 345br
$CuBr_2(4\text{-Mison})_2$		226s 124s 58s	276s 240w 212s 167s	338br 217w 216br 167m 70s	394m 343s

[a] Small splitting observed. [b] Strong splitting observed.

The ligands are arranged with increasing pK_a values, except for Acpy and Mison. br = broad and strong; m = medium; w = weak; sh = shoulder.

TABLE III. Description of Normal Modes in $CuX_2X'_2L_2$ under C_{2h} Symmetry.

Description	Total Degeneracy	Symmetry Species			
		A_g	B_g	A_u	B_u
2 Ligands (C_5H_5N)	54	13	14	14	13
Cu–X Stretching	2	1	0	0	1
Cu–X' Stretching	2	1	0	0	1
Cu–L Stretching	2	1	0	1	0
Cu–L Cu–X Bendings Cu–X'	9	1	2	2	4
Cu–L Waggings	6	1	2	0	3
Total Vibrational Degrees of Freedom	75	18	18	17	22

using monomers do not describe the system exactly, because the halogens are also bound to neighbouring copper atoms. However, for the Cu–L vibrations the approach to monomers seems reasonable.

It turns out that only three Cu–X vibrations can be assigned throughout this series. It is assumed that the two highest bands belong to short Cu–X vibrations and the band of lowest energy to the long Cu–X vibration.

For most compounds only three Cu–L vibrations can be assigned, being indicative of mixing between the theoretically expected Cu–L vibrations, having the same symmetry. The effect of pK_a of the ligands has been thoroughly investigated by Wong and Brewer [16]. The effect of substituting electron-attracting and electron-donating groups in the pyridine ring on the Cu–L stretching vibration is clearly seen from Table II. Examination of this Table reveals that with a few exceptions the Cu–L stretching vibration increase in the order:

$$\text{3,5-diClpy} < \text{py} < \text{3-Mepy} < \text{4-Etpy} < \text{4-Mepy} < \text{3,5-diMepy} < \text{3,4-diMepy}$$

This sequence of ligands goes parallel with the increasing pK_a values of ligands. From this sequence the Acpy and Mison compounds have been excluded, because the free ligands show a great number of absorptions, making assignments unreliable. Moreover the bulky polar substituents in these ligands are expected to influence the crystal packing significantly, and therefore also the Cu–L vibrations. Although $CuBr_2(4\text{-Vipy})_2$ has its Cu–L vibration within the series, $CuCl_2(4\text{-Vipy})_2$ deviates. This may have something to do with the fact that these two compounds are not mutually infrared isomorphous (*vide supra*). A similar sequence is found for the Cu–Cl vibrations, although the effect is small. Now the Cu–Cl stretching frequency increases with decreasing pK_a value of the ligands.

The suggestion of Wong and Brewer [16] that the influence of electron-attracting and electron-donating substituents in the ligand is similar when regarding Cu–Cl vibrations does not hold for this large class of ligands. It appears from Table II that the electrostatic (σ-donation) effect of the ligand is considerably larger than the π-back bonding contribution, at least with respect to the Cu–Cl frequency. A few other remarks concerning the assignments in Table II should be made, since some results are slightly different from the literature [20, 21]. The origin of these differences is the fact that discrimination between Cu–L and free-ligand vibrations is difficult for many ligands, making assignments ambiguous. Even when low-temperature measurements are carried out, exact assignment is difficult. We found that low-temperature spectra of our compounds did not yield much additional information, other than confirming the assignment, although most absorptions appear much sharper. The fact that reversed assignments in Table II do not allow a good comparison between the chlorides and the bromides, and between the normal and the deuterated compounds, and also yield deviations in the pK_a sequence, strengthens our choice of Cu–X and Cu–L vibrations.

Electron Spin Resonance and Ligand-field Spectra

ESR spectra of the powdered compounds have been recorded at ambient temperature and both X- and Q-band frequencies to confirm the proposed structure and yield detailed information about the geometry in the present compounds. The ESR and ligand-field data are listed in Table IV.

From the results in Table IV, it is seen that all the chloride compounds show a three g-value spectrum, characteristic for rhombic geometry [26]. The g-values have been taken from the Q-band spectra, as these are better resolved than the X-band spectra. Hyperfine splittings remain unresolved, however. The g-values of the $CuCl_2(4\text{-Etpy})_2$ compound are less anisotropic than those of the other chlorides; the reason for this is not clear.

For the bromide compounds, the X- and Q-band spectra exhibit only a single broad absorption. Due to exchange coupling between copper ions the copper hyperfine splittings remain unresolved. The fact that the bromide compounds even do not show a three g-value spectrum must also be caused by exchange coupling. A second reason may be the fact that the g-value is less anisotropic than that of the chloride compounds.

The ligand-field maxima have been included in Table IV. The bromide compounds show very similar spectra in band width, band shape and approximate band position, in agreement with a basically similar geometry around copper. The bands in the chloride compounds are rather weak and broad, furthermore

TABLE IV. ESR and Ligand Field Data of the Compounds CuX$_2$L$_2$, with X = Cl, Br and L = Substituted Pyridine. Uncertainties in the last digit are in parentheses.

Compound	ESR data			Ligand Field Data
	g_1	g_2	g_3	Maxima (kK)
CuCl$_2$(py)$_2$	2.23(1)	2.09(1)	2.07(1)	14.8(2)
CuCl$_2$(3-Mepy)$_2$	2.24(1)	2.07(1)	2.04(1)	15.2(2)
CuCl$_2$(4-Mepy)$_2$	2.24(1)	2.07(1)	2.03(1)	15.4(2)
CuCl$_2$(4-Etpy)$_2$	2.18(1)	2.13(1)	2.03(1)	14.9(2)
CuCl$_2$(4-Vipy)$_2$	2.26(1)	2.08(1)	2.04(1)	14.9(2)
CuCl$_2$(4-Acpy)$_2$	2.27(1)	2.09(1)	2.04(1)	14.2(2)
CuCl$_2$(4-Mison)$_2$	2.26(1)	2.08(1)	2.05(1)	14.4(2)
CuCl$_2$(3,4-diMepy)$_2$	2.25(1)	2.07(1)	2.04(1)	15.9(2)
CuCl$_2$(3,5-diMepy)$_2$	2.25(1)	2.08(1)	2.06(1)	15.4(2)
CuCl$_2$(3,5-diClpy)$_2$	2.23(1)	2.09(1)	2.06(1)	14.1(2)
CuBr$_2$(py)$_2$		2.13(1)^a		14.5(1)
CuBr$_2$(3-Mepy)$_2$		2.12(1)^a		14.7(1)
CuBr$_2$(4-Mepy)$_2$		2.11(1)^a		14.7(1)
CuBr$_2$(4-Etpy)$_2$		2.12(1)^a		14.7(1)
CuBr$_2$(4-Vipy)$_2$		2.12(1)^a		14.6(1)
CuBr$_2$(4-Acpy)$_2$		2.13(1)^a		14.4(1)
CuBr$_2$(4-Mison)$_2$		2.12(1)^a		14.5(1)
CuBr$_2$(3,4-diMepy)$_2$		2.13(2)^b		14.7(1)
CuBr$_2$(3,5-diMepy)$_2$		2.13(1)^a		14.7(1)
CuBr$_2$(3,5-diClpy)$_2$		2.12(1)^a		14.0(1)

^{a}Isotropic g-values; line widths vary from 500–800 G. ^{b}There appeared to be a small anisotropy in the g-value.

the compounds differ slightly in the position of the band maxima.

It is well known that the position of the band maximum is a function of both the spectrochemical position of the surrounding atoms and the distortion from octahedral geometry [26]. The observed band maxima all fall between the 16.0 and the 14.0 kK, corroborating with a distorted octahedral geometry [26].

Magnetic Susceptibility Measurements

The relevant data of the susceptibility measurements are listed in Table V. The values for the susceptibility are corrected for diamagnetism of constituent atoms, using Pascal's constants [27], and for temperature independent paramagnetism [28]. The appearance of a broad maximum in the susceptibility curves provides evidence for the presence of anti-ferromagnetically coupled linear-chain systems. To describe the experimental susceptibility data, a model has to be selected. Jotham [9] has shown that the anisotropic Ising simplification of the Heisenberg exchange Hamiltonian (anisotropic coupling) is substantially in error for the description of one-dimensional polymeric systems having large exchange interactions. In addition, a single-crystal magnetic susceptibility study [29] of the linear-chain complex Cu(NO$_3$)$_2$(pyrazine)$_2$ has demonstrated that, for the small J value $J = -3.7$ cm^{-1}, the exchange interaction is quite isotropic. The Heisenberg approximation was therefore chosen to describe the experimental magnetic susceptibilities.

For some compounds, however (see Table V), it was not possible to describe the data with the Heisenberg model, and in those cases we also tried to describe the data with the Ising model.

Fisher [10] published the closed form expressions for the anisotropic susceptibility of one-dimensional Ising chains of $S = \frac{1}{2}$ ions. From the expressions for the parallel susceptibility $\chi_{/\!/}$ and the perpendicular susceptibility $\chi_\perp$ the magnetic data were tried to fit with the value $\chi_{\text{powder}} = \chi_{/\!/}/3 + 2\chi_\perp/3$.

Although closed-form expressions for the magnetic susceptibility of an isotropically coupled linear Heisenberg chain anti-ferromagnet are not available, the results of Bonner and Fisher [8] for infinite chains enable us to calculate the exchange constants. They calculated the anti-ferromagnetic susceptibilities for isotropic Heisenberg coupling in zero field for finite rings up to 11 spins of $S = \frac{1}{2}$. From these calculations they extrapolated the place of the maximum and the height of the maximum susceptibility for an infinite chain:

$$\chi_{m_{\text{max.}}} = 1.282\ |J|/k \qquad \text{(a)}$$

$$\chi_{m_{\text{max.}}} = 0.07346\ N g^2 \beta^2/|J| \qquad \text{(b)}$$

From these two equations two independent J

TABLE V. Susceptibility Data for Compounds CuX_2L_2, With X = Cl, Br and L = Substituted Pyridine. Uncertainties in the last digit are in parentheses.

Compound	$T_{max.}$ (K)	$\chi_{m_{max.}}$ (emu/mol)	$-J^a$ (cm^{-1})	$-J^b$ (cm^{-1})	g^c	$\bar{g}^d$	Heisenberg fit		Curie Temperature A(K)
							$-J$ (cm^{-1})	g	
$CuCl_2py_2$	16.6(3)	0.0094(2)	9.0(2)	9.2(2)	2.10(5)	2.13(1)	9.2(2)	2.12(1)	11(2)
$CuCl_2$(3-Mepy)$_2$	14.3(3)	0.0107(2)	7.8(2)	8.0(2)	2.09(5)	2.12(1)	8.1(1)	2.14(1)	9(2)
$CuCl_2$(4-Mepy)$_2$	14.2(3)	0.0116(2)	7.7(2)	7.4(2)	2.16(5)	2.12(1)	7.3(2)	2.12(1)	7(1)
$CuCl_2$(4-Etpy)$_2$	12.6(3)	0.0130(2)	6.8(2)	6.6(2)	2.15(5)	2.11(1)	6.9(2)	2.15(1)	7(1)
$CuCl_2$(4-Vipy)$_2$	14.8(5)	0.0109(2)	8.0(2)	8.0(3)	2.13(7)	2.13(1)	8.4(2)	2.15(1)	8(1)
$CuCl_2$(4-Acpy)$_2$	14.5(3)	0.0106(2)	7.9(2)	8.2(2)	2.09(5)	2.13(1)	8.2(2)	2.13(1)	8(1)
$CuCl_2$(4-Mison)$_2$	15.8(3)	0.0098(2)	8.6(2)	8.9(2)	2.10(5)	2.13(1)	9.0(2)	2.14(1)	10(2)
$CuCl_2$(3,4-diMepy)$_2$	14.0(3)	0.0108(2)	7.6(2)	8.0(2)	2.07(5)	2.12(1)	7.9(2)	2.11(1)	9(2)
$CuCl_2$(3,5-diMepy)$_2$	16.2(4)	0.0096(2)	8.8(2)	9.1(2)	2.10(5)	2.13(1)	9.0(2)	2.11(1)	12(2)
$CuCl_2$(3,5-diClpy)$_2$	20.0(5)	0.0080(2)	10.8(4)	10.9(4)	2.12(6)	2.13(1)	11.0(2)	2.13(1)	14(2)
$CuBr_2py_2$	32 (1)	0.0058(1)	17.3(6)	15.0(7)	2.3 (1)	2.13(2)	16.6(3)	2.24(1)	e
$CuBr_2$(3-Mepy)$_2$	23.0(6)	0.0070(2)	12.5(4)	12.3(5)	2.14(8)	2.12(2)	f	f	40(9)
$CuBr_2$(4-Mepy)$_2$	19.0(6)	0.0072(2)	10.3(4)	11.8(5)	1.97(8)	2.11(2)	f	f	25(5)
$CuBr_2$(4-Etpy)$_2$	23.0(6)	0.0063(2)	12.5(4)	13.7(5)	2.03(8)	2.12(2)	13.0(2)	2.07(1)	30(6)
$CuBr_2$(4-Vipy)$_2$	26 (1)	0.0061(1)	14.1(5)	14.1(6)	2.12(9)	2.13(2)	14.2(2)	2.13(1)	50(9)
$CuBr_2$(4-Acpy)$_2$	32 (1)	0.0049(1)	17.3(7)	17.7(8)	2.10(8)	2.13(2)	17.4(3)	2.12(1)	e
$CuBr_2$(4-Mison)$_2$	33 (1)	0.0047(1)	17.9(7)	18.3(8)	2.12(8)	2.12(2)	18.4(3)	2.12(1)	e
$CuBr_2$(3,4-diMepy)$_2$	28 (1)	0.0060(1)	15.2(6)	14.5(7)	2.18(9)	2.13(3)[g]	f	f	36(9)
$CuBr_2$(3,5-diMepy)$_2$	37 (2)	0.0038(1)	20 (1)	23 (1)	2.0 (1)	2.13(2)	21.3(4)	2.07(1)	e
$CuBr_2$(3,5-diClpy)$_2$	39 (2)	0.0037(1)	21 (1)	23 (1)	2.0 (1)	2.12(2)	22.7(4)	2.11(1)	e

[a] From $T_{max.}$ [b] From $\bar{g}$, $T_{max.}$ and $\chi_{m_{max.}}$. [c] From $T_{max.}$ and $\chi_{m_{max.}}$. [d] Average experimental g value. [e] Could not be obtained due to non-linearity in $1/\chi_m$ *versus* T curve in our temp. region. [f] No clear fit could be obtained. [g] Small an-iso-tro-py in the g value.

values can be obtained. The first value is obtained from the experimental ESR g value, defined as: $\bar{g} = ((g_1^2 + g_2^2 + g_3^2)/3)^{1/2}$. It is also possible to calculate an experimental g value from expressions (a) and (b). Bonner and Fisher [8] also plotted an extrapolated susceptibility curve for the infinite chain of S = ½ ions. The experimental curves were tried to fit with the extrapolated theoretical curve graphically.

In the high-temperature region, above about 50K, our susceptibility curves obey Curie–Weiss relations, with a negative asymptotic Curie temperature A, in agreement with anti-ferromagnetism. For the chloride compounds the A values occur in the 7–14K region, for the bromide compounds in the 25–50K region. A small rise in susceptibility at very low temperatures due to paramagnetic impurities has been found for several cases. In those cases assumption of the presence of impurities up to 1% was necessary to fit the low temperature part of the curves with the Heisenberg model. For the chloride compounds the fits for the Heisenberg model are fair except for the 4-Mepy compound, as illustrated in Figure 2. For this compound also the Ising fit was very poor, suggesting that an anti-ferromagnetic inter-chain interaction cannot be ignored. In Figure 3 a plot of data for 3,5-diClpy is shown; the Heisenberg fit is reasonable. The bromine series revealed more problems, since the compounds of 3-Mepy, 4-Mepy and 3,4-diMepy could be fitted neither with the Heisenberg model nor with the Ising model. These compounds exhibit an anisotropy somewhat intermediate between the two extreme models of Ising and Heisenberg. Jeter and Hatfield [7] found the same for the $CuBr_2(py)_2$ compound. For this compound a reasonable fit within the Heisenberg model was found. Here, however, the g value used was remarkably high ($\bar{g}$ = 2.13 and g(fit) = 2.24). Examination of Table V reveals the influence of the different ligands on the exchange constants of both the chlorides and bromides. For all ligands the exchange interaction increases when the chloride is replaced by the bromide. Hatfield and coworkers [6, 7] found a similar increase for the pyridine and also for the nicotinamide, isonicotinamide and pyrazinamide compounds.

The small differences in the substituents of the pyridine molecule cause different manners of packing of the chains and this influences bond lengths and bridge angles within the chains. In Table VI, the available structural and magnetic data of compounds of our series are listed; the J values listed in the Table are very close to those published by Hatfield and coworkers [6, 7]. From this Table a clear correlation between the Cu–X–Cu bridge angle and the J value, as observed for hydroxo-bridged dimers [30], seems absent.

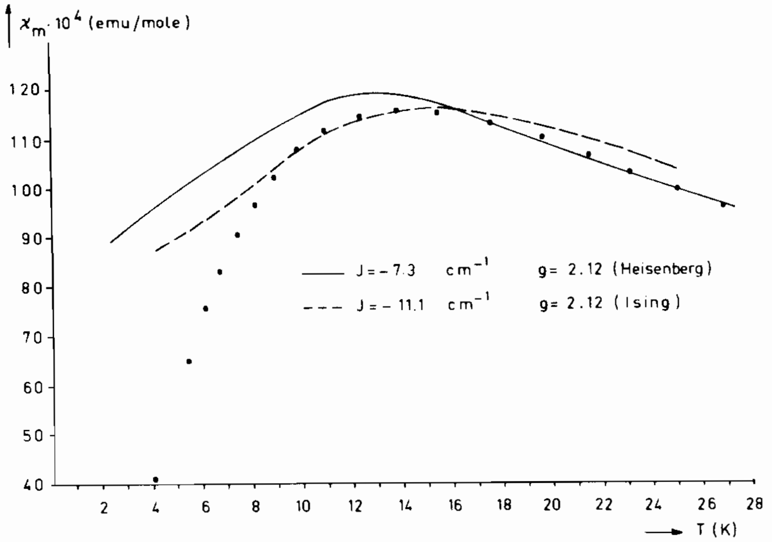

Figure 2. Molar susceptibility χ_m of $CuCl_2(4\text{-Mepy})_2$ as a function of temperature; • = experimental points. The full curve represents the theoretical fit for J = −7.3 cm^{-1} and g = 2.12 according to the results of Bonner and Fisher. The dotted curve represents the theoretical fit for J = −11.1 cm^{-1} and g = 2.12 according to Fisher's results.

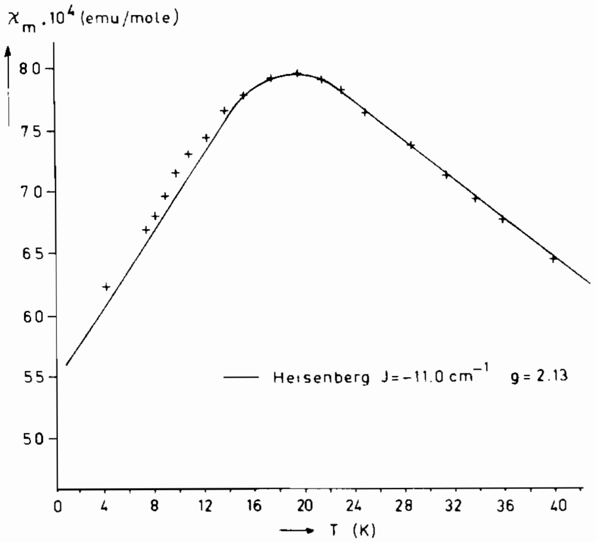

Figure 3. Molar susceptibility χ_m of $CuCl_2(3,5\text{-diClpy})_2$ as a function of temperature; + = experimental points. The full curve represents the theoretical fit for J = −11.0 cm^{-1} and g = 2.13 according to the results of Bonner and Fisher.

It appears that the length of the largest Cu–X distance influences the exchange constant to a great extent (see next section). Sources of the observed anisotropy are the dipolar interaction (especially between copper atoms in the chain), and spin–orbit coupling. For symmetry reasons anti-symmetric exchange vanishes. Within our series the anisotropy due to dipolar interaction and spin–orbit coupling are both very small compared to the observed J values. However, interchain coupling can play an important role here. Although the superexchange path goes along the chemical chain (the halogen atoms), it is difficult to deduce to what extent the ligands play a role in the superexchange mechanism. Magnetic measurements on single crystals could give more information about the exchange anisotropy. Unfortunately, large enough single crystals could not yet be prepared for this type of compounds.

Relation between Structural and Magnetic Parameters

Recently, Hatfield and coworkers [30] published a study of the structural and magnetic properties of di-μ-hydroxo-copper(II) dimers; they found a linear relationship between the Cu–O–Cu bridge angle and the exchange parameter, J.

For the linear chain compounds CuX_2L_2 we tried to find out if any structural relationship exists with the exchange constant. In the chloride series, as has already been mentioned, there are three compounds for which a single crystal structure determination has been published [1, 3, 4]. In Table VI the structural data of these compounds have been collected, together with the J values published by Hatfield and coworkers [6, 7] and the J values calculated from our measurements. In Figure 4 the long Cu–Cl bond length is plotted against the J values determined from our measurements. By plotting the Cu–Cu distance, instead of the long Cu–Cl distance, against the J value a similar plot is obtained.

This long Cu–Cl bond is correlated with the lowest Cu–Cl vibration in the far-infrared. Clearly the length of the bond is strongly related to its vibration frequency, so this frequency can be regarded as a measure of the bond length. In Figure 5 the averaged J values from Table VI are plotted against the long Cu–Cl vibration of the corresponding compounds. In the

TABLE VI. Magnetic and structural data of CuX_2L_2 compounds. Uncertainties in the last digit are in parentheses.

Compound	CuX (Å)		CuCu (Å) separation	Cu–X–Cu bridge-angle	J (cm^{-1})		Refs.
	long	short			our value[a]	lit. value	
$CuCl_2(py)_2$	3.03	2.30	3.85	92°	– 9.2(2)	– 9.15	1, 7
$CuCl_2$(4-Vipy)$_2$	3.10	2.38	3.91	90°	– 8.2(2)	– 7.8	4, 6
$CuCl_2$(4-Etpy)$_2$	3.21	2.28	4.00	92°	– 6.8(2)	– 6.7	3, 6
$CuBr_2(py)_2$	3.24	2.45	4.05	93°	–16 (1)	–18.9	2, 7

[a] Averaged J-value from Table V.

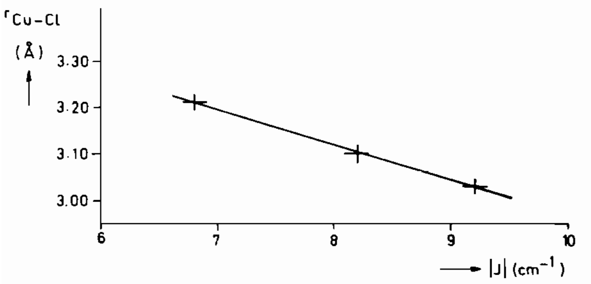

Figure 4. Plot of the long Cu–Cl bond length r_{Cu-Cl} against the |J| value for the compounds $CuCl_2$(4-Etpy)$_2$, $CuCl_2$(4-Vipy)$_2$ and $CuCl_2(py)_2$.

J region investigated the relationship is linear. In this figure also a plot of the long Cu–Cl frequency divided by the short Cu–Cl frequency against the J value is drawn. This was done in order to correct in some way for the influence of pK_a values on the frequency of the stretching vibrations. The 3-Mepy and 3,4-diMepy compounds fall slightly off the curve, probably this originates from a different symmetry of these ligands compared to the others. For these compounds the long Cu–Cl band is split, and for the plot we took the averaged value of this doublet. The splitting of this band in these compounds can also be explained by assuming that in these cases chains built up from

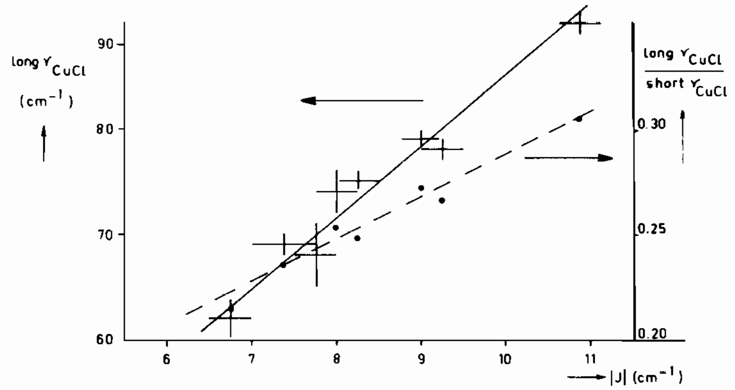

Figure 5. Plot of averaged |J| value of some compounds $CuCl_2L_2$ against the lowest Cu–Cl frequency (full curve) and against the lowest Cu–Cl frequency divided by the highest Cu–Cl frequency (dotted curve).

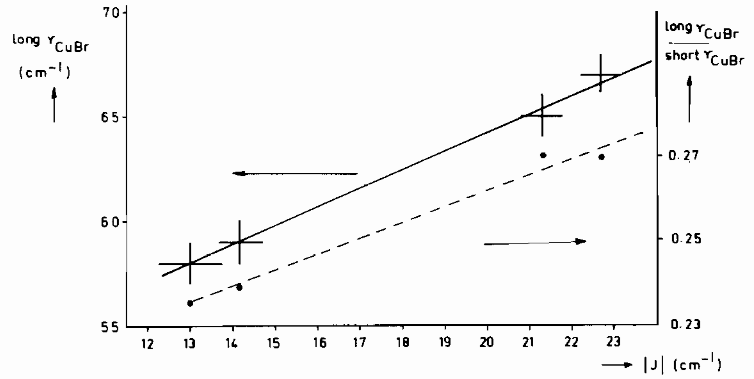

Figure 6. Plot of the |J| value of some compounds $CuBr_2L_2$ against the lowest Cu–Br frequency (full curve) and against the lowest Cu–Br frequency divided by the highest Cu–Br frequency (dotted curve).

dimeric units are present, with alternating distances between the copper ions within the chain.

Because of the uncertainty in the Cu–L vibrations the Mison and Acpy compounds were not included.

Accurate J values could not be calculated for all the bromide compounds (see magnetic measurements), therefore in Figure 6 only those J values are plotted which are obtained from reasonable fitting results, and have g values deviating only slightly from 2.13. In this figure also the "pK$_a$-corrected curve" is plotted.

Conclusions

The results of this study support the suggestion that these compounds are polymeric with considerable interaction within the chains. The magnetic interactions are antiferromagnetic in nature and the magnitude is dependent on the type and number of substituents in the pyridine ring. A comparison of the chloride and bromide compounds shows that bromide ions give rise to stronger coupling than chloride ions do. To find out which structural parameters influence the exchange constant most, precise structural data have to be awaited. A linear relationship has been found between the lowest Cu–X vibration and the J value. At present the same type of compounds but having M = Mn and Ni are under investigation. These metal ions give rise to more symmetric halogen bridges than do copper ions.

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Note added in proof (15.8.77)

After the acceptance of this paper Crawford and Hatfield (*Inorg. Chem., 16* (1977), 1336) reported magnetic measurements of similar complexes with L = py, 3-Mepy, 3-Etpy, 4-Mepy, 4-Etpy and 4-Vipy. The data for the chlorides are very similar, whereas our J-values for the bromides are slightly smaller. The deviating behaviour of the 4-Mepy chloride is explained by an alternating chain of dimers, which indeed might be the case, regarding the broad and split far-IR band centered at 69 cm^{-1}.