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Low Temperature Magnetic Behavior of Some Polymeric Divalent Copper Complexes of Common Endo-Bidentate Ligands

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The temperature dependences of the molar magnetic susceptibility of powder samples of Cu(ethylenediamine)Cl$_2$, Cu(ethylenediamine)(NCS)$_2$ and the corresponding mono-2,2'-bipyridyl analogues have been determined over the range 1.2 to 300K. All four systems exhibit weak antiferromagnetic exchange such that their Néel temperatures are $\leqslant$1.2K. There is no evidence of significant low dimensionality magnetic interactions. These results are discussed in terms of the known structures of the ethylenediamine compounds and the probable structures of the corresponding 2,2'-bipyridine systems.

Introduction

There have been a number of recent investigations of polymeric transition metal complexes containing linear or near linear chain arrays of metal atoms [1, 2]. The magnetic dilution of the arrays is such that many of these systems closely approximate one dimensional (1-D) magnetic systems. Some examples of linear chain ferro-magnets (positive intra-chain exchange J) are the *trans* bis-pyridyl polymers [M(py)$_2$X$_2$] where X is a halogen or pseudohalogen and M is Fe, Co or Ni [3–5]. In this same series the divalent Mn and Cu systems constitute Heisenberg linear chain anti-ferromagnets [6–8]. All of these systems ultimately order three dimensionally as antiferromagnets when the interchain exchange (J') becomes comparable to kT. The hallmark of linear chain (1-D) antiferromagnetism is the observation of a broad maximum in χ'_M at temperatures $T \sim J/k$. In the cases of Cu(py)$_2$Cl$_2$ and the corresponding bromide, this maximum occurs at ~13K and 27K respectively [9]. Even weaker 1-D antiferromagnetic exchange is thought to occur in the chain Cu(N$_2$H$_4$)$_2$(SO$_4$)$_2$; a SO_4^{2-} bridged polymer with axially coordinated hydrazinium cations. This system just barely shows a maximum in χ'_M at ~2K [10]. On the other hand, very strong linear chain 1-D antiferromagnetism is apparently exhibited [11] by $CuC_2O_4 \cdot 1/3\,H_2O$ for which a maximum in χ'_M is observed at $T \sim 260K$, *i.e.* $J \sim -180\ cm^{-1}$.

Certain ligands such as the exo-bidentate pyrazine force the *linear chain* structure. Thus, the monopyrazine complexes Cu(pyrazine)X$_2$ (X = Cl^-, Br^-, NO_3^-) are linear chains with moderately strong intrachain coupling (J/k varying from ~ -5 to -25 °K) [12, 13]. There have been few detailed magnetic studies of chain polymers based on common endo-bidentate ligands *e.g.* ethylenediamine, 1,10-*ortho*-phenanthroline or 2,2'-bipyridine. The *cis* coordination of the nitrogen atoms of such ligands can result in a distinctly step like, zig-zag metal atom array if all X groups are bridging. However, as will be seen for Cu(en)Cl$_2$ and Cu(en)(NCS)$_2$ (en = ethylenediamine), all X groups need not be bridging and a magnetically more dilute chain system results. It is the purpose of this article to compare the magnetic properties of such systems of known structure to those of the corresponding 2,2'-bipyridyl analogues.

Experimental

Syntheses

The systems investigated were synthesized as described in the literature [14] and gave the expected analytical results as tabulated in Table I. The analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Chemalytics Co., Tempe, Arizona.

Magnetic Susceptibility Measurements

Variable temperature magnetic susceptibility measurements were made on a Faraday balance composed of a Cahn RG electrobalance, a Varian Model 4000 electromagnet with four inch constant force pole caps and a Janis Super Vari-Temp. cryostat over the range 1.2 to 300K for ten fields between 1.6 and 5.1kG. Temperature measurement and control was typically of the order ±0.01K or better and was achieved using a Leeds-Northrup K-5 potentiometer and Lake Shore Cryotronics Model DT-500C set point controller respectively in conjunction with a

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TABLE I. Analytical Data.

Compound	Calculated %			Observed %		
	C	H	N	C	H	N
1. Cu(ethylenediamine)(NCS)$_2$	20.03	3.36	23.36	19.46	3.28	22.91
2. Cu(ethylenediamine)Cl$_2$	12.34	4.15	14.40	12.58	4.16	14.59
3. Cu(2,2'-bipyridine)(NCS)$_2$	42.91	2.40	16.68	42.88	2.61	16.56
4. Cu(2,2'-bipyridine)Cl$_2$	41.33	2.78	9.64	41.47	2.74	9.39
5. Cu(2,2'-bipyridine)Br$_2$	31.64	2.13	7.38	31.28	2.32	7.13

calibrated silicon temperature sensor diode, a ten micro-amp constant current source and an uncalibrated gallium arsenide control diode. Final temperature equilibration and stability were continuously monitored on a Leeds-Northrup Speedomax-XL 600 millivolt recorder that was used to read the error signal of the calibrated silicon diode after cancellation by the K-5 potentiometer. Temperatures below 4.2K were measured via the vapor pressure of helium using Wallace-Tiernan models FA-160 and 61-050 absolute pressure gauges while pumping was precisely controlled with an L. J. Engineering Model 329 vacuum regulator valve. Temperatures between 78K and 50K were achieved by pumping on liquid nitrogen (Welch 1397) to well below the triple point on solid nitrogen. Both the vapor pressure of nitrogen and a calibrated silicon diode were used to monitor the temperature. An F. W. Bell Model 610 Gaussmeter with a transverse Hall probe was used for measurement of magnetic field. The Faraday balance was calibrated using Hg Co(NCS)$_4$ [15–17].

ESR Spectra

ESR Spectra were determined at ambient temperature on a Bruker Instruments Model ER-10 spectrometer calibrated relative to the center of the hyperfine pattern of divalent manganese in plasticene.

Infra-Red Spectra

Infra-Red Spectra in the range 4000 to 200 cm^{-1} were determined on a Perkin-Elmer Model 567 spectrometer. Samples were in the form of standard KBr pellets or mineral oil mulls on polyethylene plates.

Results

The temperature dependences of χ'_M, μ_{eff} and χ'^{-1}_M for the CuII polymers are shown in Figures 1 through 4 while sample moment and susceptibility data are given in Tables II through VI. The Curie–Weiss Law parameters obtained from least squares computer fits of the reciprocal susceptibility *versus* temperature are given in Table VII. Some general comments are now in order. The high temperature magnetic moments of Cu(bipy)Cl$_2$, Cu(en)Cl$_2$ and Cu(en)(NCS)$_2$ are only slightly above the spin-only value of $\sqrt{3}$ expected for a ground state spin doublet and suggest relatively low

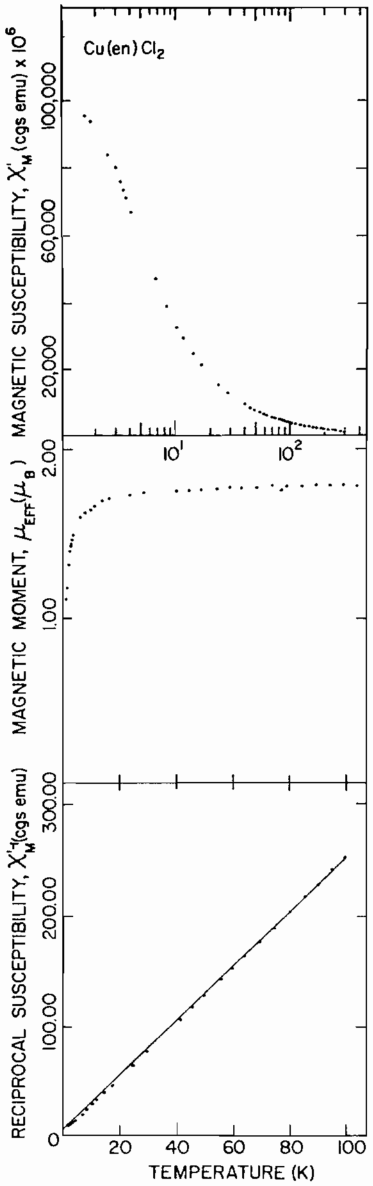


Figure 1. Magnetic data (χ'_M, χ'^{-1}_M, μ_{eff}) for Cu(en)Cl$_2$.

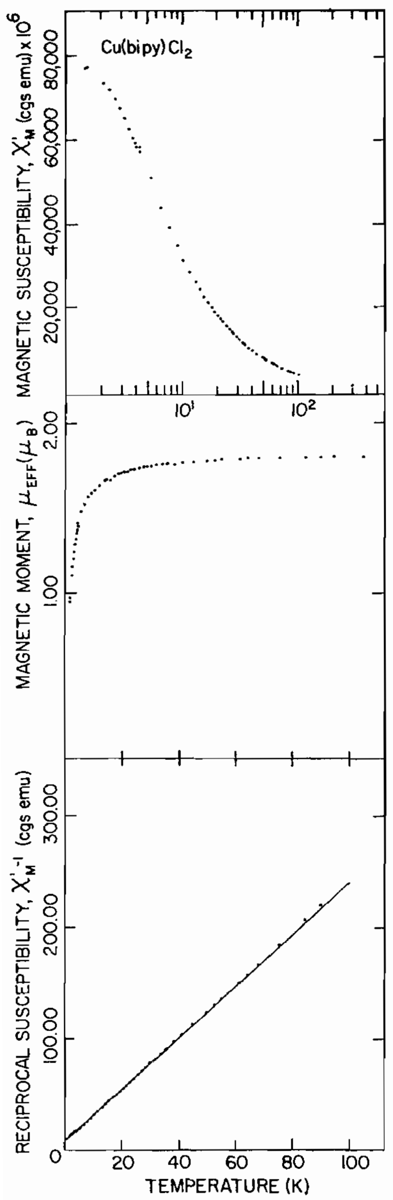


Figure 2. Magnetic data (χ'_M, χ'^{-1}_M, μ_{eff}) for Cu(bipy)Cl_2.

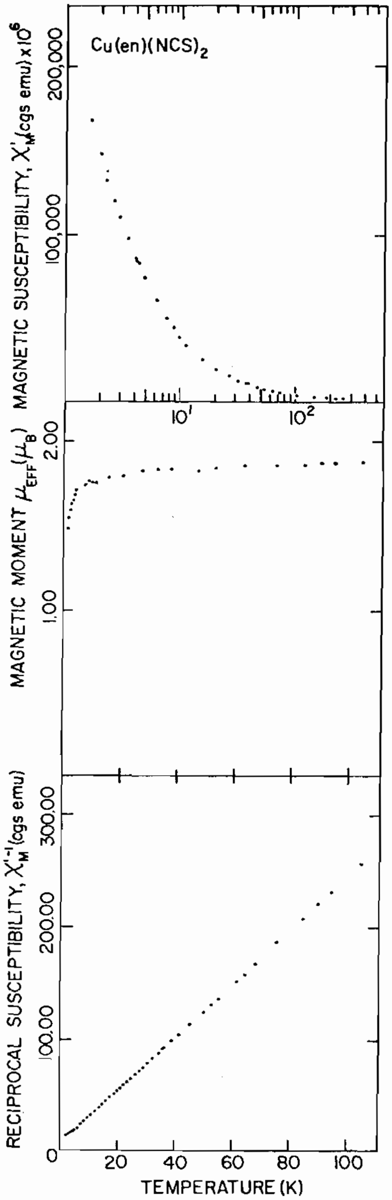


Figure 3. Magnetic data (χ'_M, χ'^{-1}_M, μ_{eff}) for Cu(en)$(NCS)_2$.

symmetry coordination environments and little residual orbital contribution to the magnetic moment. At the lowest temperatures the moments for both of the thiocyanates are ~1.5μ_B while those of Cu(en)Cl_2 and Cu(bipy)Cl_2 approach ~1.10μ_B and 0.95μ_B respectively. These values are well below the spin-only and are consistent with definite, although weak, anti-ferromagnetic exchange interaction between copper atom centers. While the susceptibility of Cu(bipy)Br_2 was determined over a somewhat more limited temperature range (300 to 78K), the moment variation suggests stronger anti-ferromagnetic exchange in the bromide complex.

All of the complexes obey a Curie–Weiss Law save Cu(bipy)$(NCS)_2$ over much of the temperature range involved. Below ~5K deviation from Curie–Weiss behavior is evident for the ethylenediamine complexes. The small negative paramagnetic Curie temperatures (θ) corresponding to the foregoing fits indicate weak anti-ferromagnetism evident in the moment behavior. The low temperature susceptibilities are field independent for ten fields varying from 1.6 to 5.1kG. In the case of Cu(bipy)$(NCS)_2$ general non-Curie–Weiss behavior is believed due to structural phase transformation(s) and the presence of more than one structural species at higher temperatures.

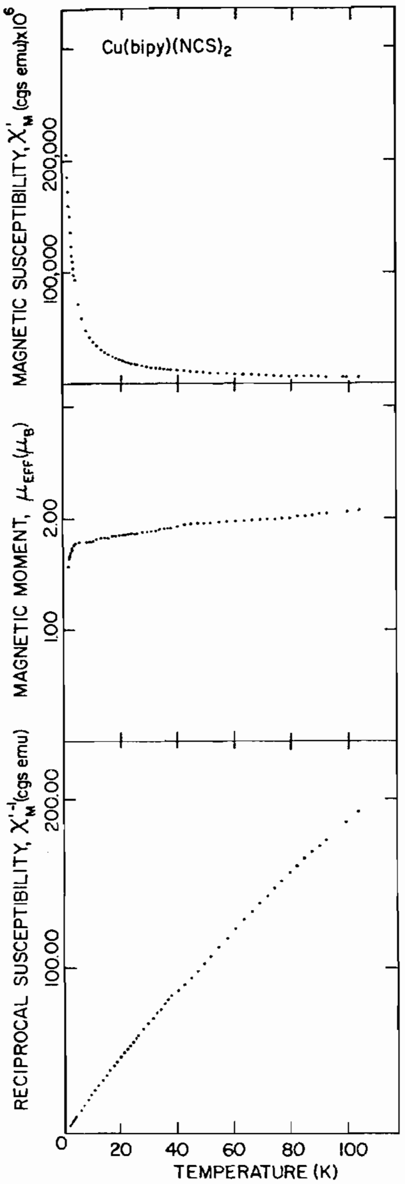


Figure 4. Magnetic data (χ'_M, χ'^{-1}_M, μ_{eff}) for Cu(bipy)(NCS)$_2$.

The latter is indicated in an extensive study [18] of the series M(bipy)(NCS)$_2$ (M = Mn, Fe, Co, Ni and Cu), using X-ray, calorimetric, Mössbauer spectroscopic, and magnetic techniques and which is the subject of a future publication.

Logarithmic plots of χ'_M *versus* T for the chlorides show that χ'_M is approaching a maximum for T $\leqslant$ 1.5K. For all ten fields the susceptibility values for Cu(bipy)Cl$_2$ actually reach a maximum at 1.52K and then begin to decrease. However, we soon reach the limit of our low temperature capability. In the case of the thiocyanate systems, there is no evidence of χ'_M approaching a maximum. From this observation and the moment-temperature variation, it is clear that although generally weak, the exchange is stronger for the chloride complexes than the corresponding thiocyanate systems. It is evident that any three dimensional magnetic ordering is such that $T_{Néel} \lesssim$ 1.5K.

TABLE II. Cu(2,2'-bipyridine)Cl$_2$.

T(K)	χ'_M	μ_B
302.90	1421	1.86
104.41	3899	1.80
75.14	5379	1.80
61.13	6604	1.80
49.48	8028	1.78
38.21	9963	1.75
29.93	12754	1.75
24.15	15487	1.73
21.54	17139	1.72
19.29	18846	1.71
16.89	21238	1.69
15.43	22432	1.66
11.76	28123	1.63
10.33	31253	1.61
7.86	38649	1.56
5.41	50306	1.48
4.29	57918	1.41
3.93	58815	1.36
3.47	61930	1.31
3.19	64480	1.28
2.87	66738	1.24
2.61	68711	1.20
2.33	70677	1.15
2.08	72639	1.10
1.52	76232	0.96
1.46	75928	0.94

TABLE III. Cu(ethylenediamine)Cl$_2$.

T(K)	χ'_M	μ_B
303.12	1377	1.83
198.45	1986	1.78
126.60	3156	1.79
95.04	4130	1.77
77.96	4910	1.75
45.24	8439	1.75
29.32	12854	1.74
24.28	15340	1.73
17.10	21384	1.71
11.75	29182	1.66
10.37	32594	1.64
8.46	38932	1.62
6.84	46488	1.59
4.21	65498	1.48
3.80	69640	1.45
3.60	72077	1.44
3.36	75002	1.42
3.06	79145	1.39
2.60	83279	1.32
1.87	92280	1.18
1.64	94219	1.11

TABLE IV. Cu(2,2′-bipyridine)$(NCS)_2$.

T(K)	χ'_M	μ_B
301.24	2491	2.45
264.09	2819	2.44
227.12	3014	2.34
187.54	3407	2.26
126.04	4452	2.12
92.37	5694	2.05
74.17	6762	2.00
49.37	9769	1.96
34.02	13385	1.91
15.92	26240	1.83
10.73	37645	1.80
3.76	103664	1.77
3.51	109986	1.76
3.28	115216	1.74
2.74	136149	1.73
2.47	150106	1.72
2.25	159697	1.70
2.03	172343	1.67
1.84	185426	1.65
1.51	205477	1.58

TABLE V. Cu(ethylenediamine)$(NCS)_2$.

T(K)	χ'_M	μ_B
265.71	1894	2.01
188.66	2423	1.91
104.64	4190	1.87
63.54	6738	1.85
53.34	7924	1.84
47.22	8781	1.82
32.55	12060	1.77
20.94	19126	1.79
11.51	33259	1.75
8.93	43359	1.76
7.70	48912	1.74
4.42	82754	1.71
4.12	85528	1.68
3.51	97399	1.65
3.01	110029	1.63
2.63	119878	1.54
2.27	131496	1.55
2.02	147418	1.54
1.65	166872	1.48

In addition there are no obvious 1 or 2 dimensional magnetic interactions in terms of broad maxima in χ'_M at higher temperatures. As mentioned earlier, in $Cu(py)_2Cl_2$ and $Cu(py)_2Br_2$ such one dimensionality is clearly evident in broad maxima in the range 18 to 40K [9], although three dimensional ordering is again seen only at very low temperatures [7, 8], 1.14K for $Cu(py)_2Cl_2$. We now discuss our observations for the present endobidentate ligand systems in terms of (a) the known structures of the ethylenediamine complexes, (b) the structure possibilities we consider for the 2,2′-bipyridine analogues, and (c) the susceptibility behavior of the other CuII polymer systems.

TABLE VI. Cu(2,2′-bipyridine)Br_2.

T(K)	χ'_M	μ_B
303.10	1978	2.19
258.21	2100	2.08
220.65	2230	1.98
188.55	2366	1.89
160.34	2530	1.80
139.69	2686	1.73
118.49	2911	1.66
104.94	3095	1.61
91.07	3340	1.56
78.37	3630	1.51

TABLE VII. Results of Least Squares Fits of χ'^{-1}_M *vs.* T to Curie–Weiss Laws.

Compounds	$\chi'_M = C/T - \theta$		
	C(e.m.u/mol)	θ(K)	μ_{eff}
$Cu(en)Cl_2$	0.413	−3.85	1.82
$Cu(en)(NCS)_2$	0.449	−2.34	1.90
$Cu(bipy)Cl_2$	0.434	−9.91	1.87

Discussion

Structure and Magnetic Exchange for $Cu(en)Cl_2$ and $Cu(en)(NCS)_2$

Figures 5 and 6 are computer generated representations of the contents of the unit cell for $Cu(en)Cl_2$ and $Cu(en)(NCS)_2$ based on the published atomic coordinates of the X-ray structure determinations

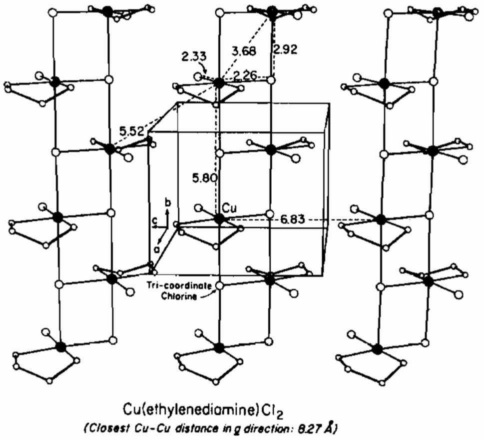
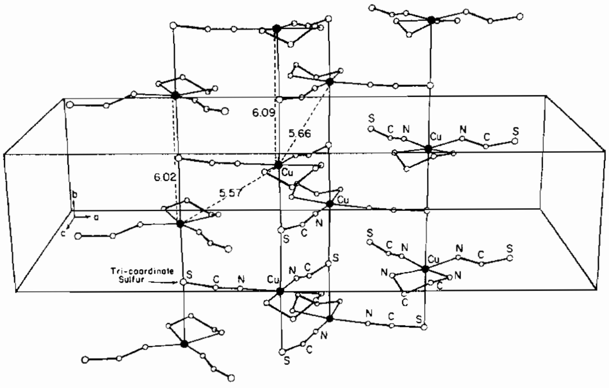


Figure 5. Unit cell structure of $Cu(en)Cl_2$.



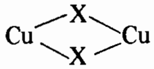
Cu(ethylenediamine)(NCS)$_2$

Figure 6. Unit cell structure of Cu(en)(NCS)$_2$.

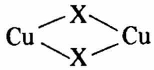
[19, 20] of these compounds. These structures are helpful in understanding the magnetic properties of the compounds of this work. In addition, we show them in detail because as will be discussed for the case of Cu(en)Cl$_2$, the original structure presentation [19] is not clear and has led to subsequent misinterpretation in published (spectroscopy) studies [14, 21] of the compound.

From Figures 5 and 6, it is evident that Cu(en)Cl$_2$ and Cu(en)(NCS)$_2$ are chlorine and sulfur bridged Cu(II) polymers. In the case of Cu(en)Cl$_2$, all Cu(II) ions are equivalent with *half* of the chlorine atoms bridging and exhibiting unusual *three coordination* while the other half are non-bridging terminal in nature. The thiocyanate compound likewise contains tri-coordinate bridging sulfur [20]. However, this complex is somewhat more complicated in that it has two inequivalent Cu atoms associated with two types of chain, one containing only terminal thiocyanate and the other all bridging. In Cu(en)Cl$_2$ the endo-bidentate ligand is coordinated so as to *alternate* from one side to the other of the polymer proceeding along the b axis. This enhances the inter-polymer chain separation (>8 Å along the a axis). The comparable distance in Cu(en)(NCS)$_2$ (along the c axis) is also large at 12.4 Å. These observations suggest considerable magnetic dilution *vis à vis* extended three dimensional magnetic ordering. A possible specific interchain interaction in Cu(en)Cl$_2$ is Cl...H-amino hydrogen bonding. However, the Cl–N orientation would appear to preclude strong interactions of this type. In any event, the results of this work indicate the sum total of such interactions results in very weak, if any, interchain exchange. In Cu(en)(NCS)$_2$ there is thiocyanate bridging between linear Cu–S–Cu–S chains throughout the entire structure. However, this three atom bridging does not result in long range magnetic ordering.

To summarize, the ethylenediamine systems can be regarded as containing Cu–Cl–Cu–Cl and Cu–S–Cu–S chains. However, *all* bridging atoms of these chains are three coordinate. We believe that the apparent lack of strong 90°



or near linear ---Cu–X–Cu–X–Cu--- interactions is related to weaker metal–chlorine (sulfur) bonding and magnetic exchange for such three coordinate bridge groups. It is expected that the pairwise



interactions are weaker for the thiocyanate than the chloride in view of the three atom bridge in the former.

Structure and Magnetic Exchange in Cu(bipy)Cl$_2$ and Cu(bipy)(NCS)$_2$

From the present work, an important conclusion that one can reach regarding the magnetic behavior of Cu(bipy)Cl$_2$ and Cu(bipy)(NCS)$_2$ is that they closely mirror their ethylenediamine analogues. To our knowledge, no single crystal X-ray structure determination has been made for either of the bipyridine complexes. One is tempted to assign these materials essentially the same basic structure possessed by the ethylenediamine systems, *i.e.* chain polymers with half of the anions bridging and half terminal. We now discuss the available published e.s.r., near infra-red, visible, and infra-red spectral data bearing on the structures of these compounds. We shall also consider some alternative, fully bridged, structure possibilities in an attempt to arrive at the most probable structure(s) for the 2,2′-bipyridine compounds.

Procter and co-workers [14] have carried out the foregoing spectroscopic studies of the chlorides and thiocyanates of the present investigation as well as the bromides. For the most part the e.s.r. and optical spectra of the ethylenediamine and bipyridine complexes are quite similar. On this basis they assign as the most probable *local coordination environment* for Cu(bipy)X$_2$ (X = Cl$^-$, Br$^-$, NCS$^-$) and Cu(en)X$_2$ either (a) tetragonal elongated octahedron or (b) square pyramidal. In their investigation these workers reference the single crystal structure determination [19] of Cu(en)Cl$_2$. The local Cu(II) environment of this system is roughly choice (a). However, they apparently misinterpret the published structure results in that they state that "each chloride ion acts as a bridging ligand with unequal bond lengths" of 2.3 Å and 2.9 Å. Examination of Figure 5 shows that this is clearly not the case. The distances just mentioned are shown in the figure and refer to only the single bridging (tri-coordinate) chloride ion. Procter *et al.* were apparently unaware of the X-ray structure determination [20] of Cu(en)(NCS)$_2$ as they did not reference it in their study. In any event, the local coordination in Cu(en)(NCS)$_2$ is also essentially choice (a). The room temperature e.s.r. results [14] for the divalent copper ethylenediamine (bipyridine) chlorides and thiocyanates may be summarized as follows: the g values ($g_{\|}$ and $g_{\perp}$) are generally in the range 2.04 to 2.30 with no absorptions at higher or lower magnetic field values. The e.s.r. spectra are consistent with magnetically dilute Cu(II) environments and rule out significant copper–copper exchange interaction (at room temperature) such as is found in many simple copper dimers. These results are in accord with the high temperature susceptibility data of the present work. It is interesting to note that the e.s.r. results of Procter *et al.* for Cu(en)Br$_2$ and Cu(bipy)Br$_2$ indicate definite, stronger magnetic exchange interactions in the bromides relative to the preceding chlorides. This also parallels the results of our more limited study of Cu(bipy)Br$_2$. It appears that for homologous series of compounds such as Cu(py)$_2$X$_2$ (X = Cl, Br) [9], Cu(pyrazine)X$_2$ [13], Cu(en)X$_2$ and most probably Cu(bipy)X$_2$ of this work, the bromides generally exhibit stronger antiferromagnetic exchange.

To our knowledge, the most detailed infra-red studies of di-imine compounds such as those considered herein are those of Wilde *et al.* [22, 23], for the series M(di-imine)X$_2$, M = Mn, Fe, Co, Ni and Cu; di-imine = 2,2′-bipyridine or 1,10-*ortho*-phenanthroline and X = Cl, Br. These workers do not consider the possibility of both bridging and terminal metal–halogen vibrations as, for example, must occur in the case of Cu(en)Cl$_2$. Thus for M(di-imine)Cl$_2$, M = Mn, Fe, Co, Ni, a single relatively strong infra-red band at ~300 cm^{-1} is attributed to the M–N stretch while the M–bridging halogen vibrations are generally ~<200 cm^{-1}. However, for the copper system they observe two vibrations near 300 cm^{-1} (305 and 295 cm^{-1} in Cu(bipy)Cl$_2$) both of which are again attributed to M–N stretching vibrations while the Cu–bridging chlorine occurs at 173 cm^{-1}. The appearance of two metal–nitrogen vibrations for the copper systems and not for any of the other compounds is attributed to Jahn–Teller distortion in the former. We have also determined the infra-red spectrum of Cu(bipy)Cl$_2$ over the range 250 to 500 cm^{-1} and find essentially the same band pattern, *i.e.* a band at 309 and one at 292 cm^{-1}. By analogy with Cu(en)Cl$_2$, we believe that it is more likely that one of the foregoing absorptions is, in fact, a Cu–Cl (terminal) vibration rather than both Cu–N. In our determination of the far-infrared spectrum of Cu(en)Cl$_2$, we observe a strong broad band at 319 cm^{-1} as well as a strong band at 220 cm^{-1} that we assign to the terminal and bridging Cu–Cl respectively. As perhaps expected, we do not observe the strong transition at 220 cm^{-1} in the far infrared spectrum of Cu(en)(NCS)$_2$.

The foregoing analogy between copper 2,2′-bipyridine and ethylenediamine systems of identical stoichiometry is not unreasonable. A good precedent for this is found in Cu(en)SO$_4$·2H$_2$O and Cu(bipy)SO$_4$·2H$_2$O. Single crystal X-ray structure determinations [24, 25] show these compounds to have nearly identical sulfato bridged chain polymer structures. Thus in view of the magnetic data of this work, our analysis of the far-infrared spectra, the similarity of optical and especially e.s.r. spectra [14] and finally, the preceding analogy, we suggest that the structures of Cu(bipy)Cl$_2$ and Cu(bipy)(NCS)$_2$ are essentially the same as the ethylenediamine analogues. The X-ray structure determinations of the ethylenediamine compounds clearly illustrate tri-coordinate bridging sulfur and chlorine. This unusual structural unit has been incorrectly suggested *as unique* in a recent [26] X-ray investigation of the structures of dibromo[2-(2-aminomethyl)pyridine]copper(II) and dibromo(2-methyl-1,2-diaminopropane)copper(II) by Helis, *et al.* The earlier X-ray studies of Cu(en)Cl$_2$ and Cu(en)(NCS)$_2$ as well as the preceding work of Helis *et al.* indicate that tri-coordinate bridges may be the rule of copper polymers involving single endobidentate ligands. This allows for six coordination with four short and two long bonds, a bonding pattern common to divalent copper. *Fully bridged* structure possibilities such as shown in Figure 7 would be expected to lead to stronger magnetic exchange interactions in terms of stronger super-exchange pathways between pairs of metal atoms. Our studies [27] indicate that such structures are most likely the case for M(di-

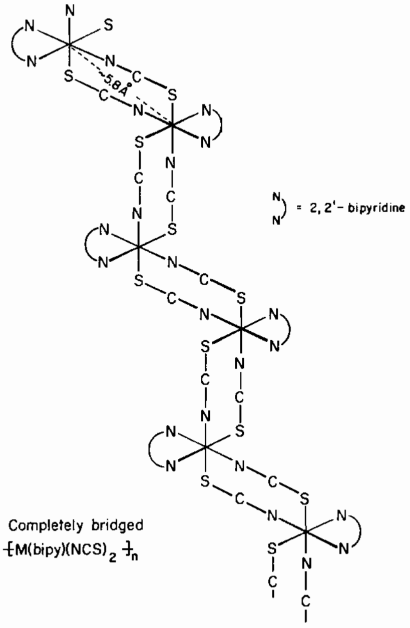


Figure 7. A possible structure for a completely bridged M(bipy)(NCS)$_2$ system.

imine)X_2 systems where M = Mn, Fe, Co, Ni, and X = Cl^-, Br^-, NCS^-. In the cases of Fe and Ni, the exchange interactions are very strongly ferromagnetic, and there is no evidence of terminal (non-bridging) halogen for any of these systems.

We conclude this investigation by pointing out that three distinct types of magnetic behavior (*vis à vis* strength of exchange interactions) have now been experimentally observed for divalent copper–organo ligand chain polymers. These are:

(I) Relatively strong, distinguishable 3D and 1D antiferromagnetic interactions as found in Cu(pid)Br_2 and Cu(pht)Br_2 (pid = pyridazine, pht = phthalazine) for which 1D and 3D maxima in χ'_M occur at ~55 and 12K and ~60 and 15K respectively [28, 29];

(II) Strong 1D and weak 3D antiferromagnetic interactions as found in $Cu(py)_2X_2$ (X = Cl^-, Br^-) [9] and Cu(pz)X_2 (X = Cl^-, Br^-, NO_3^-) [12, 13];

(III) Weak 1D and 3D interactions as found in the polymers of common endo-bidentate ligands in this study and $Cu(N_2H_5)_2(SO_4)$ [10, 30].

Acknowledgments

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