Synthetic, Structural, and Spectroscopic Studies on Copper(II), Copper(I), and Silver(I) Complexes of a Series of Pyridazinophane and Phthalazinophane Macrocycles. Unusual Extended Metallocyclic Structures

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A series of new (2:2) phthalazinophane (S_4, S_6) and (1:1) pyridazinophane (S_4, S_8) macrocyclic ligands and some of their complexes with Cu(II), Cu(I), and Ag(I) are described. The ligands are characterized by ^{1}H NMR and mass spectrometry and in one case by X-ray crystallography, and the complexes, by infrared, electronic, and electron spin resonance spectra and in some cases by X-ray crystallography. The complex $[Cu(L1)Br]_x$ (I) (L1 = 1:1 macrocycle from reaction of 3,6-dichloropyridazine and 1,4,8,11-tetrathiaundecane) crystallized in the monoclinic system, space group $P2_1/c$ with $a = 9.140(3)$ Å, $b = 13.939(7)$ Å, $c = 13.115(5)$ Å, $\beta = 106.77(4)°$, and $Z = 2$. The structure was refined to $R = 0.032$ and $R_w = 0.029$ for 2015 unique reflections with $I > 3.00\sigma(I)$. The ligand coordinates in an *exo*-bidentate fashion, linking Cu_2Br_2 units via two aliphatic thioether sulfur atoms in an interlocked, two-dimensional "zigzag" latticework. $[Cu_{1.5}(L3)Cl_{1.5}]_x$ (II) (L3 = 1:1 macrocycle from reaction of 1,4-dichlorophthalazine and 1,4,8,11-tetrathiaundecane) crystallized in the triclinic system, space group $P\bar{1}$ with $a = 12.150(4)$ Å, $b = 18.760(3)$ Å, $c = 8.700(3)$ Å, $\alpha = 91.27(2)°$, $\beta = 107.69(2))°$, $\gamma = 87.87(2)°$, and $Z = 2$. The structure was refined to $R = 0.035$ and $R_w = 0.034$ for 4614 unique reflections with $I > 3.00\sigma(I)$. The overall structure of **II** is that of an infinite double-stranded polymer, with two *exo*-bidentate, macrocyclic, S_2 ligands bridging the trinuclear chloro-bridged copper centers. To our knowledge this is the first example of a polynuclear copper(I) halide complex with trinuclear repeating units. $[C_{15}H_{18}S_4N_2]$ (L3) crystallized in the monoclinic system, space group $P2_1/n$, with $a = 8.827(2)$ Å, $b = 11.461(2)$ Å, $c = 16.197(2)$ Å, $\beta = 98.27(2)°$, and $Z = 4$. The structure was refined to $R = 0.033$ and $R_w = 0.028$ for 2021 unique reflections with $I > 2.00\sigma(I)$.

Introduction

Tetradentate (N_4) pyridazine and phthalazine ligands produce predominantly dinuclear copper(II) complexes,[1] some of which exhibit quite positive, reversible, and quasireversible one-electron reduction steps (per metal).[2–8] Catalytic effects for the aerial oxidation of catechols have also been shown.[4] The evolution of this type of ligand to include combinations of diazine and thioether donors, which might provide a more thermodynamically viable redox process and perhaps lead to more efficient catalysis, has led us to explore the copper coordination chemistry of a variety of macrocyclic thioether–diazine ligands, e.g pyridazinophanes and phthalazinophanes. Our initial studies in this area have involved the synthesis and characterization of a series of macrocyclic thioether–pyridazine ligands and their Cu(II), Cu(I), and Ag(I) complexes.[9–11] A variety of mononuclear and polynuclear copper(II) derivatives were produced in which, in most instances, only pyridazine nitrogen coordination occurred. However one polymeric derivative involved N_2S_2 coordination to copper(II) centers. The copper(I) and silver (I) complexes studied so far are polymeric species involving just sulfur coordination.

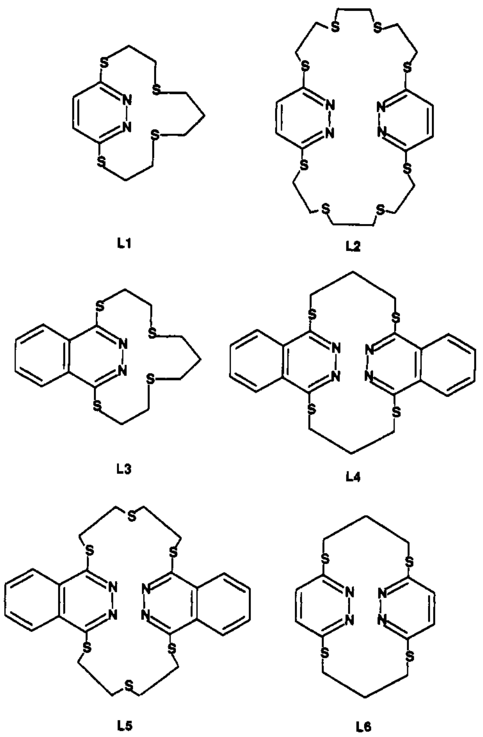

Figure 1. Structural representation of the ligands.

The present study describes the copper(II), copper(I), and silver(I) coordination chemistry of a series of 1:1 and 2:2 macrocycles (Figure 1) involving pyridazine and phthalazine

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subunits, with S_2, S_3, and S_4 linkages between diazine groups, including three new phthalazinophane ligands.

Experimental Section

Commercially available reagents (Aldrich) were used without further purification. Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FT-IR instrument. Electronic spectra were recorded as mulls using a Cary 5E spectrometer. The ESR spectra were recorded with a Bruker ESP 300 X-band spectrometer at room temperature and 77 K. Mass spectra were obtained using a VG Micromass 7070 HS spectrometer, and NMR spectra, using a GE 300-MHz instrument. X-ray diffraction data were collected using a Rigaku AFC6S instrument, and magnetic susceptibility data were measured by the Faraday method using a Cahn 7600 magnetic susceptibility system. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, British Columbia, Canada.

Synthesis of Ligands and Complexes. The synthesis of L1 has been reported.[10]

L2. 1,4,7,10-Tetrathiadecane[12] (2.70 g, 12.5 mmol) was added to anhydrous ethanol (100 mL), in which sodium metal (0.575 g, 25.0 mmol) had been dissolved, and the resulting solution was stirred for 20 min. 3,6-Dichloropyridazine (1.92 g, 12.5 mmol) was dissolved in anhydrous ethanol (100 mL) and both solutions were added dropwise, simultaneously, to refluxing anhydrous ethanol (500 mL) by using pressure-equalizing funnels, under a dry nitrogen atmosphere. The addition took place over a period of 6 h, during which time a pale yellow precipitate formed. The mixture was stirred and refluxed for a further 2 h and then stirred at room temperature overnight. The solid was filtered off, washed with anhydrous ethanol, and deionized water, dried in vacuo, and recrystallized from $CHCl_3$ and then $MeNO_2$. White crystals of L2 were obtained. Yield: 0.86 g (24%). Mp: 206–208 °C. ^1H NMR ($CDCl_3$) (δ (relative intensity)): 3.02 (16) (multiplet, CH_2), 3.55 (8) (multiplet, CH_2), 7.24 (4) (singlet, pyridazine). Mass spectrum, major mass peaks (*m/e* (relative intensity)): 580 (1.4) P, 521 (10), 461 (9), 291 (19), 231 (19), 170 (49), 144 (4), 87 (92), 60 (100).

L3. 3,7-Dithianonane-1,9-dithiol[13] (2.28 g, 10.0 mmol) was added to anhydrous ethanol (100 mL) in which sodium metal (0.46 g, 20.0 mmol) had been dissolved, and the resulting solution was stirred for 30 min. 1,4-Dichlorophthalazine (1.99 g, 10.0 mmol) was then dissolved in anhydrous THF (100 mL) and both solutions were simultaneously added dropwise to refluxing anhydrous THF (500 mL), by using pressure-equalizing funnels under an atmosphere of dry nitrogen, over a period of 6 h. The mixture was then stirred under reflux overnight. The solvent was removed on a rotary evaporator, the residue was dissolved in $CHCl_3$, the extract was washed with water, dried over anhydrous Na_2SO_4, and filtered, and the filtrate was concentrated to about 50 mL, whereupon white crystals formed. Yield: 1.56 g (44%). Mp: 228–230 °C. ^1H NMR ($CDCl_3$) (δ (relative intensity)): 2.00 (2) (multiplet, CH_2), 2.81 (4) (triplet, CH_2), 2.91 (4) (multiplet, CH_2), 3.60 (4) (multiplet, CH_2), 7.85 (2) (multiplet, phthalazine), 8.00 (2) (multiplet, phthalazine). Mass spectrum, major mass peaks (*m/e* (relative intensity)): 354 (17) P, 321 (6), 252 (10), 194 (69), 133 (100), 120 (34), 105 (24), 87 (15).

L4 and L5 were prepared in a similar manner by using 1,3-propanedithiol and 2-mercaptoethyl sulfide, respectively. L4: colorless crystals; yield 48%. Mp: 263–265 °C. ^1H NMR ($CDCl_3$) (δ (relative intensity)): 2.40 (4) (multiplet, CH_2), 3.54 (8) (multiplet, CH_2), 7.75 (4) (multiplet, phthalazine), 7.98 (4) (multiplet, phthalazine). Mass spectrum, major mass peaks (*m/e* (relative intensity)): 468 (94) P, 435 (14), 266 (37), 201 (54), 129 (100), 106 (55). L5: white crystals; yield 36%. Mp: 270–272 °C. ^1H NMR ($CDCl_3$) (δ (relative intensity)): 3.19 (8) (multiplet, CH_2), 3.82 (8) (multiplet, CH_2), 7.77 (4) (multiplet, phthalazine), 8.03 (4) (multiplet, phthalazine). Mass spectrum, major mass peaks (*m/e* (relative intensity)): 560 (0.3) P, 501 (50), 474 (29), 253 (24), 194 (83), 129 (29), 87 (100).

$[Cu(L1)Br]_x$ (I) and $[Cu_{1.5}(L3)Cl_{1.5}]_x$ (II). Cu powder (190 mg, 3.0 mmol) was added to a solution of $CuBr_2$ (96.0 mg, 0.4 mmol) in CH_3CN (20 mL). The mixture was stirred for 6 h under a nitrogen atmosphere and the resulting colorless solution filtered into a solution of L1 (91.2 mg, 0.3 mmol) in $CHCl_3$ (20 mL) under a nitrogen atmosphere. The resulting pale yellow solution was left at room temperature for several days and colorless crystals of **I** formed. Yield: 53 mg (79%). **II** was prepared in a similar manner as yellow crystals.

$Ag(L3)ClO_4$ (III). A solution of L3 (53 mg, 0.15 mmol) in $CHCl_3$ (10 mL) was added to a solution of $AgClO_4$ (63 mg, 0.30 mmol) in CH_3CN (10 mL). The combined solution was filtered, and the filtrate was allowed to stand at room temperature overnight. Pale yellow crystals formed, which were filtered off, washed with CH_3CN, and dried in air. Yield: 62 mg (74%). Recrystallization from CH_3CN caused the complex to decompose, giving the ligand. Anal. Calcd for $C_{15}H_{18}N_2S_4AgClO_4$: C, 32.06; H, 3.23; N, 4.99. Found: C, 32.04; H, 3.24; N, 5.00.

$Cu(L2)Cl_2{\cdot}THF$ (IV), $Cu(L4)Cl_2$ (V), $Cu(L4)(NO_3)_2{\cdot}0.5H_2O$ (VI), and $Cu(L5)Cl_2{\cdot}0.5H_2O$ (VII). To prepare **IV**, L2 (92.0 mg, 0.16 mmol) dissolved in THF (40 mL) was added to a solution of $CuCl_2{\cdot}2H_2O$ (85.0 mg, 0.50 mmol) in THF (20 mL). The resulting dark green solution was filtered, and the filtrate was allowed to stand at room temperature overnight. Brown crystals formed, which were filtered off, washed with $CHCl_3$ and CH_3CN, and dried in air. Yield: 72 mg (57%). Anal. Calcd for $C_{20}H_{28}S_8N_4CuCl_2{\cdot}THF$: C, 36.60; H, 4.61; N, 7.11. Found: C, 36.90; H, 4.88; N, 7.00. **V** and **VI** were prepared in a similar way as bright green crystals. **VII** was obtained as yellowish green crystals. Anal. Calcd for $C_{22}H_{20}N_4S_4CuCl_2$ (**V**): C, 43.81; H, 3.34; N, 9.29. Found: C, 43.42; H, 3.37; N, 9.30. Calcd for $C_{22}H_{20}N_4S_4Cu(NO_3)_2{\cdot}0.5H_2O$ (**VI**): C, 39.72; H, 3.18; N, 12.63. Found: C, 39.91; H, 3.13; N, 12.31. Calcd for $C_{24}H_{24}N_4S_6CuCl_2{\cdot}0.5H_2O$ (**VII**): C, 40.92; H, 3.58; N, 7.96. Found: C, 40.77; H, 3.40; N, 7.80.

Crystallographic Data Collection and Refinement of the Structures. (a) $[Cu(L1)Br]_x$ (I). Crystals of **I** are colorless. The diffraction intensities of an approximately 0.250 × 0.250 × 0.200 mm crystal were collected with graphite-monochromatized Mo Kα radiation with a Rigaku AFC6S diffractometer, using the ω–2θ scan mode to $2\theta_{max} = 50.0°$. Cell constants and the orientation matrix were obtained by the least-squares refinement of the setting angles of 23 carefully centered reflections in the range $20.42 < 2\theta < 25.22°$. A total of 3138 reflections were collected, of which 2948 were unique ($R_{int} = 0.077$) and 2015 were considered significant with $I_{net} > 3.00\sigma(I_{net})$. An empirical absorption correction was applied, using the program DIFABS,[14] which resulted in transmission factors ranging from 0.55 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[15,16] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2015 observed reflections ($I > 3.00\sigma(I)$) and 173 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum(|F_o| - |F_c|)/\sum(|F_o|) = 0.032$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2} = 0.029$, with weights based on counting statistics, and included a factor ($\rho = 0.01$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and –0.50 electron/Å^3, respectively, and have no chemical significance. Neutral-atom scattering factors[17] and anomalous dispersion terms[18,19] were taken from the usual sources. All calculations were performed with the TEXSAN[20] crystallographic software package using a VAX 3100 workstation. Hydrogen atoms were located in a difference map but not refined. Thermal parameters were set at 1.2 times the isotropic thermal parameters of the bonded C atoms.

A summary of crystal and other data is given in Table I, atomic positional parameters are given in Table II, and selected bond distances and angles are given in Table V. Thermal parameters (Table S1), hydrogen atom parameters (Table S2), and complete bond distances and angles (Table S3) are deposited as supplementary material.

(b) II. The same procedures were used for this compound. Crystal and other data are given in Table I. Atomic positional parameters are given in Table III, and selected bond angles and distances are listed in Table VI. Thermal parameters (Table S4), hydrogen atom positional parameters (Table S5), and complete bond distances and angles (Table S6) are deposited as supplementary material.

(c) L3. The same procedures were used for L3. Hydrogen atoms were located from a difference map and their positions allowed to refine.

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Table I. Summary of Crystal, Intensity Collection, and Structure Refinement Data for **I**, **II**, and L3

	I	**II**	L3
formula	$C_{22}H_{32}S_8Cu_2Br_2N_4$	$C_{30}H_{36}S_8N_4Cu_3Cl_3$	$C_{15}H_{18}S_4N_2$
fw	895.90	1006.12	354.56
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	9.140(3)	12.150(4)	8.827(2)
b (Å)	13.939(7)	18.760(3)	11.461(2)
c (Å)	13.115(5)	8.700(3)	16.197(2)
α (deg)		91.27(2)	
β (deg)	106.77(4)	107.69(2)	98.27(2)
γ (deg)		87.87(2)	
V (Å^3)	1600(1)	1887.9(9)	1621.6(5)
d_{calcd} (g cm^{-3})	1.860	1.770	1.452
Z	2	2	4
abs coeff, μ (cm^{-1})	43.32	23.51	5.57
radiation, λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69
T (°C)	25	25	25
R	0.032	0.035	0.033
R_w	0.029	0.034	0.028

[a] $R = \sum(|F_o| - |F_c|)/\sum(|(F_o|)$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

Table II. Final Atomic Positional Parameters and B(eq) Values (Å^2) for $[Cu(L1)Br]_x$ (**I**)

atom	x	y	z	B(eq)[a]
Br(1)	0.14813(6)	–0.10046(4)	0.56222(4)	3.50(2)
Cu(1)	0.07652(8)	0.01806(4)	0.41226(5)	3.19(3)
S(1)	0.0500(1)	–0.07444(9)	0.2608(1)	2.82(5)
S(2)	–0.3003(1)	–0.39991(9)	0.0783(1)	2.77(5)
S(3)	–0.5923(2)	–0.2365(1)	–0.1931(1)	3.05(5)
S(4)	–0.2175(1)	0.12158(9)	0.0078(1)	2.83(5)
N(1)	–0.4130(4)	–0.1320(3)	–0.0376(3)	2.5(2)
N(2)	–0.3312(4)	–0.0533(3)	0.0066(3)	2.5(2)
C(1)	–0.1143(6)	–0.1520(3)	0.2463(4)	2.9(2)
C(2)	–0.1307(6)	–0.2321(3)	0.1638(3)	2.7(2)
C(3)	–0.2682(6)	–0.2948(3)	0.1639(4)	3.1(2)
C(4)	–0.3697(6)	–0.3480(3)	–0.0523(4)	2.6(2)
C(5)	–0.5361(5)	–0.3153(3)	–0.0783(4)	2.9(2)
C(6)	–0.4890(5)	–0.1318(3)	–0.1402(3)	2.3(2)
C(7)	–0.4914(6)	–0.0526(4)	–0.2058(4)	2.9(2)
C(8)	–0.4096(6)	0.0258(3)	–0.1611(4)	2.9(2)
C(9)	–0.3294(5)	0.0231(3)	–0.0527(3)	2.3(2)
C(10)	–0.1320(5)	0.0729(3)	0.1405(4)	2.7(2)
C(11)	–0.0090(5)	–0.0009(3)	0.1413(4)	2.7(2)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}\,\mathbf{a}_i{}^*\mathbf{a}_j{}^*\bar{\mathbf{a}}_i{\cdot}\bar{\mathbf{a}}_j$.

Their thermal paramaters were set to 20% greater than their bonded partners. Atomic positional parameters are given in Table IV, and selected bond distances and angles are listed in Table VII. Thermal parameters (Table S-VII), hydrogen atom positional parameters (Table S-VIII), and complete bond distances and angles (Table S-IX) are deposited as supplementary material.

Results and Discussion

X-ray Crystal Structures. (a) L3. The placement of rigid aromatic spacers in macrocyclic thiacyclophanes leads to some dramatic changes in the conformational characteristics of macrocyclic thioether ligands and also leads to different coordination modes. A simple *o*-xylyl spacer in the potentially tridentate ligand 2,5,8-trithia[9]-*o*-benzophane (TTOB) seems to limit the conformational flexibility of the macrocyclic ring, which favors an *endo* conformation[21] in its complexes, despite the fact that the free-ligand conformation is *exo*.[22] The compound *fac*-Mo(CO)$_3$(TTOB) involves the facial coordination of the ligand as a tridentate S_3 donor.[22] This contrasts sharply with the situation for crown thioether ligands containing just aliphatic chains, where the conformations are dependent upon the structural preferences of e.g. the $-SCH_2CH_2SCH_2CH_2S-$ linkages.[23] The inclusion of a *m*-xylyl spacer appears to stiffen the ligand even more in 2,5,8-trithia[9]-*m*-benzophane (TTMB),[24] such that its coordination capacity is diminished. However it does form a palladium complex, $PdCl_2$(TTMB), in which it coordinates as an S_2 bidentate ligand with the third, uncoordinated sulfur remaining *exo*-dentate to the ring.[24] An interesting extension of this ligand by incorporation of $-(CH_2)_3-$ fragments between the thioether sulfurs created an ideal opportunity for metalation in the complex [Pd(TT[11]MC)]$^+$ (TT[11]MC = 2,6,10-trithia[11]-*m*-cyclophane).[25] The palladium is bound in a square-planar environment to the three ring sulfurs and the benzene 1-carbon.

Table III. Final Atomic Positional Parameters and B(eq) Values (Å^2) $[Cu_{1.5}(L3)Cl_{1.5}]_x$ (**II**)

atom	x	y	z	B(eq)[a]
Cu(1)	0.35185(6)	–0.21984(3)	0.20888(8)	3.26(3)
Cu(2)	0.60256(6)	–0.22833(4)	0.4214(1)	4.64(4)
Cu(3)	0.51276(6)	–0.31910(4)	0.59856(8)	4.04(3)
Cl(1)	0.3740(1)	–0.23806(7)	0.4835(2)	3.48(6)
Cl(2)	0.5411(1)	–0.17652(8)	0.1837(2)	4.54(7)
Cl(3)	0.6348(1)	–0.34931(7)	0.4471(2)	4.19(6)
S(1)	0.7363(1)	0.11376(6)	0.8805(1)	2.49(5)
S(2)	1.0848(1)	0.12606(7)	0.8196(2)	3.05(6)
S(3)	1.0314(1)	–0.19209(7)	0.6074(2)	2.93(5)
S(4)	0.6800(1)	–0.16881(7)	0.6590(2)	3.01(6)
S(5)	0.5237(1)	–0.38975(7)	0.8063(2)	3.08(6)
S(6)	0.8577(1)	–0.31525(7)	1.1328(2)	3.67(6)
S(7)	1.0088(1)	–0.63538(7)	1.2193(2)	3.18(6)
S(8)	0.6486(1)	–0.67668(6)	0.9245(2)	2.67(5)
N(1)	0.9723(3)	0.0110(2)	0.6927(5)	2.5(2)
N(2)	0.9602(3)	–0.0602(2)	0.6443(4)	2.4(2)
N(3)	0.8524(3)	–0.4520(2)	1.0546(5)	3.0(2)
N(4)	0.8869(3)	–0.5237(2)	1.0732(5)	2.8(2)
C(1)	0.8916(4)	0.1116(2)	0.9214(5)	2.6(2)
C(2)	0.9337(4)	0.1479(2)	0.7945(6)	2.8(2)
C(3)	1.0752(4)	0.0368(2)	0.7472(5)	2.2(2)
C(4)	1.1803(4)	–0.0023(2)	0.7523(5)	2.2(2)
C(5)	1.2900(4)	0.0266(3)	0.8024(6)	2.9(2)
C(6)	1.3849(4)	–0.0156(3)	0.8034(6)	3.3(2)
C(7)	1.3741(4)	–0.0870(3)	0.7582(6)	3.6(3)
C(8)	1.2677(4)	–0.1165(3)	0.7085(6)	2.9(2)
C(9)	1.1683(4)	–0.0749(2)	0.7043(5)	2.2(2)
C(10)	1.0523(4)	–0.1000(2)	0.6544(5)	2.1(2)
C(11)	0.8752(4)	–0.1952(3)	0.5590(6)	2.9(2)
C(12)	0.8334(4)	–0.1888(2)	0.7069(6)	2.7(2)
C(13)	0.6700(4)	–0.0742(3)	0.6114(6)	3.0(2)
C(14)	0.7086(4)	–0.258(2)	0.7575(6)	2.6(2)
C(15)	0.6908(4)	0.0525(2)	0.7099(6)	2.7(2)
C(16)	0.6301(4)	–0.3581(3)	0.9883(6)	2.9(2)
C(17)	0.7330(4)	–0.3228(3)	0.9558(6)	3.3(2)
C(18)	0.9111(4)	–0.4047(2)	1.1555(6)	2.6(2)
C(19)	1.0160(4)	–0.4214(3)	1.2832(6)	2.6(2)
C(20)	1.0869(5)	–0.3700(3)	1.3820(6)	3.3(2)
C(21)	1.1860(5)	–0.3916(3)	1.4980(6)	3.9(3)
C(22)	1.2166(5)	–0.4632(3)	1.5239(6)	4.2(3)
C(23)	1.1489(4)	–0.5145(3)	1.4287(6)	3.4(2)
C(24)	1.0488(4)	–0.4963(3)	1.3061(6)	2.5(2)
C(25)	0.9757(4)	–0.5430(2)	1.1941(6)	2.5(2)
C(26)	0.8894(4)	–0.6714(2)	1.0600(6)	2.8(2)
C(27)	0.7754(4)	–0.6641(2)	1.0969(6)	2.7(2)
C(28)	0.6509(4)	–0.5981(2)	0.8060(6)	2.7(2)
C(29)	0.5928(4)	–0.5337(3)	0.8580(6)	3.0(2)
C(30)	0.5970(4)	–0.4692(3)	0.7561(6)	3.0(2)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}\mathbf{a}_i{}^*\mathbf{a}_j{}^*\bar{\mathbf{a}}_i{\cdot}\bar{\mathbf{a}}_j$.

The ligands described in this report involve 1,4-spacers within the thiocyclophane ring, except that the spacers are themselves ligand groups, which have been shown in the past to be the dinucleating focus in a series of N_4 and N_6 open-chain pyridazine and phthalazines.[1–7] The 1,4-aromatic fragment in L3 forms a symmetrical pivot, about which the $-S(CH_2)_2S(CH_2)_3S(CH_2)_2S-$ loop could be considered to swing like a skipping rope. The sulfur atoms are disposed in an *exo*-dentate fashion in L3 (Figure 2),

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Table IV. Final Atomic Positional Parameters and B(eq) Values (Å^2) for L3

atom	x	y	z	B(eq)[a]
S(1)	0.82360(8)	0.39469(7)	0.48580(5)	3.16(3)
S(2)	0.55307(9)	0.10360(7)	0.35852(5)	3.26(3)
S(3)	0.09480(8)	0.11533(7)	0.56692(5)	3.07(3)
S(4)	0.32432(9)	0.40462(7)	0.71908(5)	3.25(3)
N(1)	0.4382(2)	0.3649(2)	0.5799(1)	2.8(1)
N(2)	0.5495(2)	0.3639(2)	0.5279(1)	2.7(1)
C(1)	0.4663(3)	0.4165(2)	0.6528(2)	2.6(1)
C(2)	0.6038(3)	0.4809(2)	0.6804(2)	2.4(1)
C(3)	0.6293(4)	0.5468(3)	0.7547(2)	3.2(1)
C(4)	0.7624(4)	0.6087(3)	0.7748(2)	3.8(1)
C(5)	0.8751(4)	0.6055(3)	0.7225(2)	3.8(2)
C(6)	0.8548(3)	0.5411(3)	0.6505(2)	3.2(1)
C(7)	0.7180(3)	0.4784(2)	0.6279(2)	2.4(1)
C(8)	0.6822(3)	0.4127(2)	0.5517(2)	2.4(1)
C(9)	0.7201(3)	0.3035(3)	0.4044(2)	3.0(1)
C(10)	0.6935(3)	0.1790(3)	0.4319(2)	2.9(1)
C(11)	0.3746(3)	0.1667(3)	0.3825(2)	2.9(1)
C(12)	0.3171(3)	0.1125(3)	0.4579(2)	3.0(1)
C(13)	0.1672(3)	0.1670(3)	0.4737(2)	3.0(1)
C(14)	0.2222(3)	0.1915(3)	0.6473(2)	2.8(1)
C(15)	0.1801(3)	0.3194(3)	0.6532(2)	2.8(1)

[a] $B(\text{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}\mathbf{a}_i^*\mathbf{a}_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

Table V. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in [Cu(L1)Br]$_x$ (**I**)

Br(1)–Cu(1)	2.507(1)	Cu(1)–S(1)	2.321(2)
Br(1)–Cu(1)	2.458(1)	Cu(1)–S(2)	2.315(2)

Cu(1)–Br(1)–Cu(1)	76.09(4)	Br(1)–Cu(1)–S(1)	119.40(5)
Br(1)–Cu(1)–Br(1)	103.91(4)	Br(1)–Cu(1)–S(2)	121.44(5)
Br(1)–Cu(1)–S(1)	104.15(5)	S(1)–Cu(1)–S(2)	101.11(6)
Br(1)–Cu(1)–S(2)	104.88(5)		

Table VI. Bond Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in [Cu$_{1.5}$(L3)Cl$_{1.5}$]$_x$ (**II**)

Cu(1)–Cl(1)	2.353(2)	Cu(1)–Cl(2)	2.539(2)
Cu(1)–S(1)	2.262(1)	Cu(1)–S(8)	2.239(1)
Cu(2)–Cu(3)	2.783(1)	Cu(2)–Cl(2)	2.208(2)
Cu(2)–Cl(3)	2.293(2)	Cu(2)–S(4)	2.280(2)
Cu(3)–Cl(1)	2.237(2)	Cu(3)–Cl(3)	2.313(2)
Cu(3)–S(5)	2.234(2)		

Cl(1)–Cu(1)–Cl(2)	108.53(6)	Cl(1)–Cu(1)–S(8)	111.58(6)
Cl(2)–Cu(1)–S(1)	90.43(5)	Cl(2)–Cu(1)–S(8)	96.88(6)
S(1)–Cu(1)–S(8)	129.77(6)	Cu(3)–Cu(2)–Cl(2)	136.64(5)
Cu(3)–Cu(2)–Cl(3)	53.15(4)	Cu(3)–Cu(2)–S(4)	86.04(5)
Cl(2)–Cu(2)–Cl(3)	122.17(7)	Cl(2)–Cu(2)–S(4)	124.10(6)
Cl(3)–Cu(2)–S(4)	112.23(6)	Cu(2)–Cu(3)–Cl(1)	72.42(5)
Cu(2)–Cu(3)–Cl(3)	52.51(4)	Cu(2)–Cu(3)–S(5)	154.16(5)
Cl(1)–Cu(3)–Cl(3)	114.12(6)	Cl(1)–Cu(3)–S(5)	128.09(6)
Cl(3)–Cu(3)–S(5)	116.26(6)	Cu(1)–Cl(1)–Cu(3)	113.64(6)
Cu(1)–Cl(2)–Cu(2)	79.49(6)	Cu(2)–Cl(3)–Cu(3)	74.34(5)

and this conformation is retained in **I** and **II** and also in the complex [Ag(L1)(ClO$_4$)]$_x$,[10] which involves the corresponding pyridazine ligand. A significant conformational reorganization would be necessary to bring atoms S(2) and S(3) into an *endo* conformation (S(1) and S(2) are not considered as possible donors in an intramolecular sense). However, with the presence of the nitrogen atoms on the phthalazine ring (and the pyridazine ring in L1), which are suitably disposed, according to molecular models, to allow simultaneous N$_2$S$_2$ coordination to two metal centers, it was felt that SN chelation might create a stable dinuclear species, in particular with copper(II). Such a bonding mode with ligands of this sort has, so far, not been observed. What appears to be the case for L3, and also for L1, is an *exo*-bidentate mode of coordination, which encourages the formation of most interesting polymeric derivatives, in particular with copper(I)[9] and silver(I)[10] salts.

The structure of L3 is illustrated in Figure 2, and listings of atomic distances and angles are found in Tables VII and S-IX. Sulfur–carbon distances to the phthalazine ring (1.768(3) Å) compare closely with those of open-chain, tetradentate thio–pyridazine ligands[3,26,27] and thio–phthalazine ligands.[7] Other aliphatic sulfur–carbon distances (1.809–1.822 Å) compare closely with those found in *o*- and *m*-xylyl thiacyclophane ligands[21,22,24,25] and macrocyclic thioethers.[23] The aliphatic carbon–carbon distances are considered normal for thioethers of this sort.

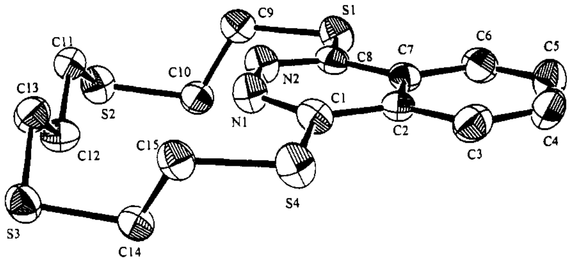

Figure 2. Molecular structure of L3 with hydrogen atoms omitted.

Table VII. Distances (Å) and Angles (deg) for L3

S(1)–C(8)	1.768(3)	N(1)–N(2)	1.383(3)
S(1)–C(9)	1.822(3)	N(1)–C(1)	1.312(3)
S(2)–C(10)	1.809(3)	N(2)–C(8)	1.306(3)
S(2)–C(11)	1.826(3)	C(9)–C(10)	1.524(4)
S(3)–C(13)	1.822(3)	C(11)–C(10)	1.522(4)
S(3)–C(14)	1.817(3)	C(12)–C(13)	1.518(4)
S(4)–C(1)	1.768(3)	C(14)–C(15)	1.519(4)
S(4)–C(15)	1.823(3)		

C(8)–S(1)–C(9)	100.4(1)	S(2)–C(10)–C(9)	112.0(2)
C(10)–S(2)–C(11)	101.6(1)	S(2)–C(11)–C(12)	114.0(2)
C(13)–S(3)–C(14)	100.5(1)	C(11)–C(12)–C(13)	111.4(3)
C(1)–S(4)–C(15)	100.5(1)	S(3)–C(13)–C(12)	115.0(2)
S(1)–C(8)–N(2)	116.9(2)	S(3)–C(14)–C(15)	112.2(2)
S(4)–C(1)–N(1)	116.9(2)	S(4)–C(15)–C(14)	113.4(2)
S(1)–C(9)–C(10)	114.0(2)		

The presence of the 1,4-heterocyclic ring within the 15-membered macrocycle confers an unusual degree of planarity to about half of the ring itself. Dihedral angles between the least-squares plane of the phthalazine itself and the planes defined by C(1)–S(4)–C(15) and C(8)–S(1)–C(9) (5.47(3) and 4.62(3)°, respectively, away from the phthalazine plane) indicate an almost planar arrangement of the heterocyclic ring and the connected carbon–sulfur bonds. This serves to preorient and effectively fix the *exo*-ligand conformation.

(b) [Cu(L1)Br]$_x$ (I). The structure of [Cu(L1)Br]$_x$ (**I**) is illustrated in Figures 3 and 4. The structure of **I** is quite different from that of its analogue [Cu(L1)Cl]$_x$.[10] In the chloro complex the ligand coordinates in an *exo*-bidentate fashion with two different, alternate ligand sulfur atoms, one adjacent to the pyridazine ring and one in the thioalkane framework, linking Cu$_2$Cl$_2$ units in a double-stranded polymeric arrangement. Each repeating unit consists of a large metallocycle with an alternating arrangement of two copper(I) pairs and two S$_2$ ligands. Figure 3 shows a fragment of the structure of **I** with a comparable Cu$_2$(μ_2-Br)$_2$ unit bonded to four ligands via sulfur donors. However in this case the macrocyclic ligands coordinate in an *exo*-bidentate fashion in a different manner, with each ligand bonded by two adjacent, aliphatic thioether sulfurs, linking the Cu$_2$Br$_2$ units in an interlocked, two-dimensional "zigzag" latticework, in which, within each strand, the ligands alternate in a pseudo-trans arrangement on the same end of the Cu$_2$Br$_2$ centers, and the Cu$_2$Br$_2$ units themselves cross-link the strands (Figure 4). The diazine ring is forced to occupy an extra-strand position, and there is no indication that the pyridazine nitrogens are involved in bonding. The repeating unit is a much bigger metallocyclic ring involving four ligands, two dinuclear centers and half of two

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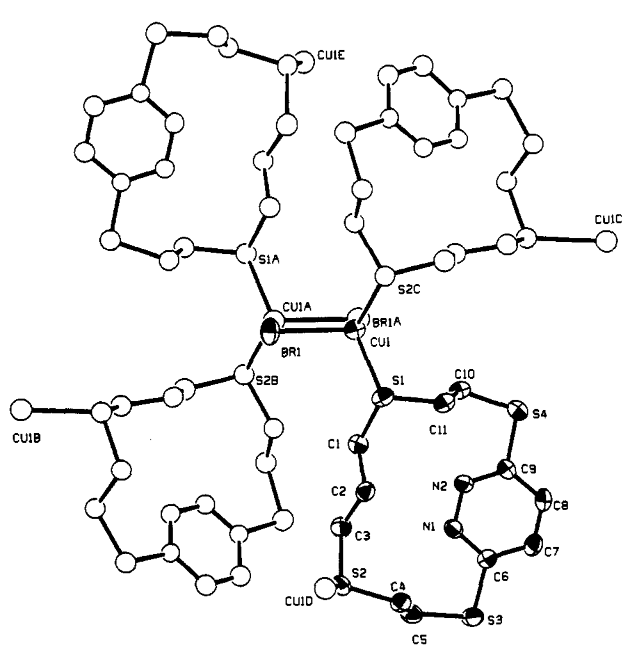

Figure 3. Molecular structure of a fragment of $[Cu(L1)Br]_x$ (I) with hydrogen atoms omitted.

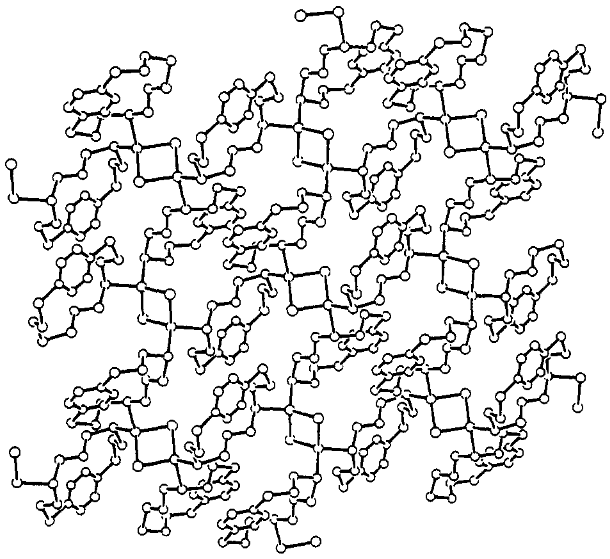

Figure 4. Extended structure of $[Cu(L1)Br]_x$ (I) showing cross-linking, with hydrogen atoms omitted.

dinuclear centers. The copper centers have approximately tetrahedral geometries, with fairly long contacts to the bridging bromine atoms (2.507(1), 2.458(1) Å) and copper–sulfur distances (Cu(1)–S(1) = 2.321(2) Å, Cu(1)–S(2) = 2.315(2) Å) that are somewhat larger than those in $[Cu(L1)Cl]_x$.[10]

Dihedral angles of 4.07(4) and 4.69(4)° between the units C(9)–S(4)–C(10) and C(6)–S(3)–C(5), respectively, and the pyridazine best plane (same side of the plane) indicate the near-planar nature of the $-(CH_2)S$–pyridazine–$S(CH_2)-$ fragment, similar to the situation observed in L3.

(c) $[Cu_{1.5}(L3)Cl_{1.5}]_x$ (II). The structure of II is illustrated in Figure 5. The overall structure is that of an infinite double-stranded polymer, with two *exo*-bidentate, macrocyclic S_2 ligands bridging the trinuclear chloro-bridged copper center. The same two adjacent aliphatic thioether sulfurs are involved in bonding. So far, few examples of trimeric Cu(I) aggregates are known,[28–33] and to our knowledge this is the first example of a polynuclear

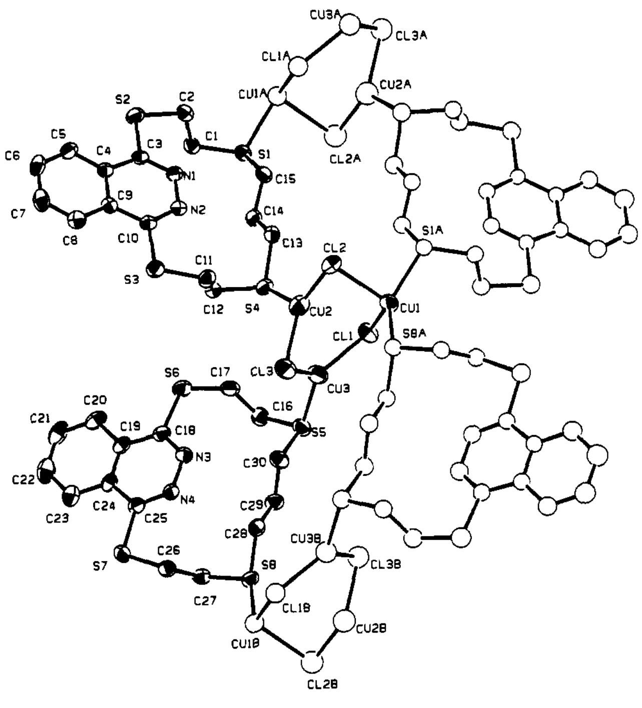

Figure 5. Molecular structure of a fragment of $[Cu_{1.5}(L3)Cl_{1.5}]_x$ (II) with hydrogen atoms omitted.

copper(I) halide complex with trinuclear repeating units. The three copper centers have different geometries and are bridged by three chlorines, forming a six-membered alternating Cu–Cl ring. Cu(1) is coordinated to two sulfur and two chlorine ligands, in a distorted tetrahedral geometry, and Cu(2) and Cu(3) are three coordinate with one sulfur and two chlorine ligands each. The three Cu- -Cu distances are quite different (Cu(1)–Cu(2) = 3.046(2) Å, Cu(2)–Cu(3) = 2.783(2) Å, Cu(1)–Cu(3) = 3.843(2) Å), resulting in a highly distorted metallocyclic ring. The very long Cu(1)–Cu(3) separation is accompanied by a very large Cu(1)–Cl(1)–Cu(3) angle (113.64(6)°), as would be anticipated. The Cu(1)–Cl(2) distance (2.539(2) Å) is somewhat larger than typical Cu–Cl separations found in comparable derivatives.[10,33]

Since L3 coordinates via two adjacent aliphatic thioether sulfur atoms, the noncoordinated phthalazine subunit is forced to orient itself on the periphery of the polymeric strand. This contrasts sharply with the structural features of $[Cu(L1)Cl]_x$[10], where in the double-stranded polymer the noncoordinating diazine rings are found within the polymeric strand. This may be associated with steric factors associated with the bulk of the fused benzene ring present in L3. The *endo-endo* coordination mode of L3 appears again to be the result of the near planarity of the $-(CH_2)S$–phthalazine–$S(CH_2)-$ fragments (dihedral angles between C–S–C(phthalazine) planes and phthalazine mean planes fall in the range 2.2–6.5°), brought about by the inclusion of the 1,4-heterocyclic fragment in the ring. The ligand conformation is largely retained in the complex.

Spectroscopy and Magnetism. The pyridazine ligands L1, L2, and L6 (Figure 1) have single, sharp infrared absorptions at 1569, 1572, and 1570 cm^{-1} respectively, associated with CN stretch in the diazine rings (Table VIII). A very small shift to lower energy (1 cm^{-1}) (Table VIII) is observed for this band in complex IV, while for I a shift of 8 cm^{-1} occurs. In previous work, shifts to

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Table VIII. Infrared, Magnetic, Electronic Spectral, and ESR Data

compd	color	IR bands (cm^{-1})	μ_{eff}(room temp) (μ_B)	UV/vis (cm^{-1})[a]	ESR[b]
[Cu(L1)Br]$_x$ (**I**)	colorless	1561 (ν(CN))			
[Cu$_{1.5}$(L3)Cl$_{1.5}$]$_x$ (**II**)	yellow	1569 (ν(CN))			
Ag(L3)ClO$_4$ (**III**)	pale yellow	1569 (ν(CN)) 1096, 1050 (ν(ClO$_4$))			
Cu(L2)Cl$_2$·THF (**IV**)	brown	1571 (ν(CN)) 307 (ν(Cu–Cl))	1.81	21 300 15 500	$g_1 = 2.04$ $g_2 = 2.06$ $g_3 = 2.19$
Cu(L4)Cl$_2$ (**V**)	bright green	1562 (ν(CN)) 298, 288 (ν(Cu–Cl))	1.78	16 200	$g_\parallel = 2.20$ $g_\perp = 2.06$
Cu(L4)(NO$_3$)$_2$ (**VI**)	bright green	1778, 1720 (ν(NO$_3$)) 1562 (ν(CN))	1.80	15 500	$g_{av} = 2.08$
Cu(L5)Cl$_2$ (**VII**)	green	1567 (ν(CN)) 320 (ν(Cu–Cl))	1.78	15 300	$g_\parallel = 2.17$ $g_\perp = 2.07$

[a] Mull transmittance. [b] Solid (room temperature). ν(CN), cm^{-1}: L1, 1569; L2, 1572; L3, 1580; L4, 1574; L5, 1572; L6, 1570.

lower energy of around 10 cm^{-1} have been associated with diazine nitrogen coordination, while much smaller negative shifts and even small shifts to higher energy have been associated with just sulfur coordination.[9–11] Compound **I** does not involve pyridazine nitrogen coordination and so it is reasonable to suggest that **IV**, which involves a 2:2 pyridazinophane macrocycle and involves a shift of ν(CN) of 1 cm^{-1} to lower energy, might be expected to involve just sulfur coordination as well. The appearance of a very strong band at 21 300 cm^{-1}, which can be assigned to S → Cu charge transfer, also supports sulfur coordination. The appearance of one strong band at 307 cm^{-1}, assigned to Cu–Cl stretch, suggests a trans CuS$_2$Cl$_2$ structure in this compound. Comparable ν(CN) bands for ligands L3, L4, and L5 are found at 1580, 1574, and 1572 cm^{-1}, respectively. A shift of 11 cm^{-1} to lower energy for **II**, which has only sulfur coordination, suggests that much larger shifts to lower energy might be expected for nitrogen coordination with the phthalazinophane macrocycles. A similar shift for **III** suggests sulfur coordination, which would be in keeping with the sulfur only structure of [Ag(L1)(ClO$_4$)]$_x$, which involved bidentate perchlorate bridges in a 2D latticework structure.[10] Two prominent perchlorate bands for **III** at 1096 and 1050 cm^{-1} suggest a low-symmetry ClO$_4^-$ group, which is possibly involved in coordination.

It is difficult to obtain unequivocal information about coordination behavior of the diazine moiety from the ν(CN) shift, and with **V** and **VI**, involving L4, it would be reasonable to assume phthalazine coordination, even though modest shifts to lower energy are observed. The absence of any low-energy charge-transfer bands in their electronic spectra (Table VIII) also would suggest phthalazine nitrogen coordination. Also the demonstrated N-coordination in the compounds [Cu(L6)Cl$_2$] (Figure 1), involving a cis CuN$_2$Cl$_2$ planar structure, and [Cu(L6)$_2$](ClO$_4$)$_2$, with a CuN$_4$ planar structure,[9] strongly suggests similar N$_2$ ligand coordination in **V** and **VI**. The presence of two bands for **V** at 288 and 298 cm^{-1} in the far-infrared suggests a cis CuN$_2$Cl$_2$ structure for this compound, and the observation of two widely separated nitrate ($\nu_1 + \nu_4$) combination bands[34] at 1720 and 1778 cm^{-1} suggests the presence of bidentate nitrates and a cis pseudooctahedral structure for **VI**. The infrared spectrum of Cu(L5)Cl$_2$ (**VII**) shows a ν(CN) band at 1567 cm^{-1}, shifted by 5 cm^{-1} to lower energy than that of the free ligand, and its electronic spectrum shows no absorption attributable to S → Cu charge transfer. In the far infrared spectrum it has only one strong band at 320 cm^{-1}, assigned to Cu–Cl stretch in a trans square-planar CuN$_2$Cl$_2$ arrangement like that of its pyridazine analogue.[11]

Room-temperature magnetic moments for compounds **IV**-**VII** (Table VIII) all exceed the spin-only value for a one-unpaired-electron system and suggest the presence of dilute Cu(II) centers in all cases. The X-band ESR spectra of the copper(II) complexes were recorded at 295 K (Table VIII) and 77 K and were similar at both temperatures. **IV** exhibits a spectrum indicative of rhombic distortion, while **V** and **VII** exhibit axial spectra. **VI** has an uninformative isotropic spectrum.

Conclusion. Unlike the situation where ortho-, and to a lesser extent, meta-aromatic spacers in a cyclophane ring encourage *endo*-dentate coordination, the inclusion of a 1,4-aromatic fragment seems to confer extra rigidity on the ring, causing a preference for *exo*-dentate coordination and the formation of unusual, extended, polymeric derivatives, at least in those cases involving small 1:1 rings. Such systems are of interest from the standpoint of their solid state properties, e.g. conductance, and, in those cases where similar structures could involve paramagnetic metal centers, extended magnetic properties. Further studies on these and related systems are ongoing.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Tables listing detailed crystallographic data, hydrogen atom positional parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares planes (25 pages). Ordering information is given on any current masthead page.

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