Pyridazine Complexes of Copper(II) Nitrate: Synthesis and Structural and Magnetic Studies

Tom Otieno, Steven J. Rettig, Robert C. Thompson,* and James Trotter

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, B.C., Canada V6T 1Z1

Received June 22, 1994[⊗]

The pyridazine (pdz) complexes [Cu(pdz)$_3$(NO$_3$)$_3$]$_2$Cu, **1**, [Cu(pdz)$_3$(NO$_3$)$_2$], **2**, [Cu(pdz)$_4$(NO$_3$)$_2$], **3**, and [Cu(pdz)$_4$(NO$_3$)][NO$_3$], **4**, have been prepared and characterized by spectroscopic methods, magnetic susceptibility measurements and, for **1** and **4**, by single crystal X-ray diffraction. **1** crystallizes in the monoclinic space group $P2_1/n$, with $a = 8.938(1)$ Å, $b = 13.6677(6)$ Å, $c = 14.933(2)$ Å, $\beta = 96.03(1)°$ and $Z = 2$. **4** crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.6425(9)$ Å, $b = 16.442(1)$ Å, $c = 11.9930(6)$ Å, $\beta = 98.225(6)°$ and $Z = 4$. Both structures were solved by the Patterson method and refined by full-matrix least-squares procedures to $R = 0.029$ and 0.034 for 3026 and 3572 reflections with $I \geq 3\sigma(I)$, respectively. **1** has a linear trimetallic structure and exhibits strong antiferromagnetic coupling. Analysis of powder susceptibility data according to a Heisenberg model yields a J value of -139 cm^{-1}. The remaining three compounds have monometallic structures and are magnetically dilute.

Introduction

There has been considerable interest in the coordination chemistry of the 1,4-diazine pyrazine (pyz), particularly in its use as a bridging ligand, and a very large number of complexes of this type has been reported in the literature.[1] Our own research on pyrazine complexes has concentrated on compounds with polymeric structures and on magnetic exchange effects.[2,3] In a review of nitrogen heterocycles as bridging ligands it was pointed out that, in contrast to the situation with pyrazine, the 1,2-diazine analogue, pyridazine (pdz), has been much less frequently studied as a bridging ligand.[1] The purpose of the present study is to investigate further the coordination chemistry of pyridazine, particularly as it relates to that of pyrazine. Such a study should permit an evaluation of the effect of changing from a potentially linear-bridging 1,4-diazine to a potentially bent-bridging 1,2-diazine on the probability of forming bridged complexes and, where bridging occurs, on structure and magnetic properties. Of importance regarding the latter, pyridazine offers a shorter two-atom pathway for exchange.

Although there have been several studies involving binucleating ligands which contain the 1,2-diazine link,[4–6] reports on complexes in which pyridazine itself acts as a bridging ligand remain relatively rare. One such complex of particular relevance to this work is Cu(pdz)Cl$_2$, the structure of which consists of an extended chain of copper ions, singly bridged by pyridazine ligands.[7] Magnetic studies on this compound and on the analogous bromo and cyanato compounds[2,8] have revealed strong antiferromagnetic interactions. These studies demonstrated that the pyridazine ligand can bridge metal ions in extended chains and can lead to stronger magnetic coupling than analogous pyrazine systems. As an extension of this work, we have undertaken a systematic study of the complexes formed between copper(II) nitrate and pyridazine. The nitrate counterion was chosen partly on the grounds that it is a more weakly coordinating ion toward copper(II) than are the cyanate or halide ions and hence should complement the earlier studies and provide new information on pyridazine coordination. In addition, results of earlier studies on the corresponding pyrazine system, which led to the structural and magnetic characterization of the extended linear chain complex Cu(pyz)(NO$_3$)$_2$,[9–13] were available for comparison with the present work.

Four complexes of composition Cu(pdz)$_n$(NO$_3$)$_2$ (n = 2, 3, and 4 (two forms)) were isolated and characterized in this work. The bis(pyridazine) complex has a novel trimetallic structure of composition [Cu(pdz)$_3$(NO$_3$)$_3$]$_2$Cu, **1**, and contains double pyridazine bridges between copper centers. Detailed magnetic susceptibility studies to cryogenic temperatures are reported for this compound. The tris(pyridazine) complex and one form of the tetrakis(pyridazine) complex have the neutral monometallic structures [Cu(pdz)$_3$(NO$_3$)$_2$], **2**, and [Cu(pdz)$_4$(NO$_3$)$_2$], **3**, respectively, while the other isolated form of the tetrakis(pyridazine) complex has the ionic formulation [Cu(pdz)$_4$(NO$_3$)][NO$_3$], **4**. The structures of **1**, **2**, and **4** were established by single crystal X-ray diffraction studies, as reported here for **1** and **4** and elsewhere for **2**.[14] Magnetic susceptibility studies and vibrational, electronic, and electron paramagnetic resonance spectroscopic studies are reported here for all four complexes and are used to obtain indirect evidence regarding the structure of **3**.

[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1995.

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0020-1669/95/1334-1718$09.00/0

Experimental Section

Syntheses. Examination of products obtained from the reaction, at room temperature, of reagent grade pyridazine and copper(II) nitrate in various molar ratios in ethanol (containing 10% v/v 2,2-dimethoxypropane (2,2-dmp)) led to the identification of four distinct products. Repeated experiments established the general conditions for obtaining these materials. Addition of pyridazine to a solution of the copper salt (pdz:Cu mole ratio in the range 1−1.5) gave a blue precipitate which on air drying yielded the green $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**. Employing higher pdz:Cu ratios in the range 2.0−2.7 gave $[Cu(pdz)_3(NO_3)_2]$, **2**, directly as a blue precipitate. The violet complex $[Cu(pdz)_4(NO_3)_2]$, **3**, was obtained by adding the copper nitrate solution slowly to pyridazine and maintaining the pdz:Cu ratio in excess of 4:1. The fourth complex, $[Cu(pdz)_4(NO_3)][NO_3]$, **4**, proved to be the most difficult to obtain. This blue complex was obtained on several occasions by employing a copper to pyridazine ratio of ~4:1 and adding the copper(II) nitrate solution to pyridazine. The difficulty is that we found these conditions sometimes produced precipitates primarily composed of **2** or **3** as identified by elemental analysis and by comparison of spectroscopic properties with authentic samples prepared as described above. Our interpretation of these findings is that the solutions in which the pdz:Cu ratio is close to 4:1 contain **3** in equilibrium with the species in which either a nitrate or a pyridazine ligand is dissociated, **4** and **2**, respectively. Once one of these species begins crystallizing from solution, the equilibrium shifts in its favor and the product is primarily that species.

Compound **1** appears to be stable indefinitely in air and no special precautions in handling it are necessary. The other three materials visibly decompose on standing even in a dry nitrogen atmosphere. Compound **2** changes color from bright (royal) blue to greenish blue on standing while **3** and **4** which when freshly prepared are violet and blue, respectively, visibly darken over time and eventually turn black. The time taken for decomposition to become noticeable did not seem to be related to whether or not the samples were exposed to the atmosphere and varied from preparation to preparation, ranging from a few days to several months. Characterizations reported here for **2**, **3**, and **4** were made on freshly prepared samples. We found that reproducible microanalytical, spectroscopic and magnetic data were obtained for these materials provided no visible signs of decomposition had occurred. The compounds were generally handled in an inert atmosphere although no such precautions were taken with the single crystal used in the X-ray analysis of **4**. Experimental details for typical preparations of each of the complexes follow.

Bis[(μ-nitrato-*O*)bis(nitrato)bis(μ-pyridazine)(pyridazine)copper(II)]copper(II), $[Cu(pdz)_3(NO_3)_3]_2Cu$, 1. Pyridazine (5.23 mmol) was slowly added to a filtered solution of copper(II) nitrate trihydrate (3.50 mmol) dissolved in 8 mL of ethanol containing 10% v/v 2,2-dmp. A blue precipitate formed. Anhydrous diethyl ether (30 mL) was added to the reaction vessel and the mixture stirred briefly. The product was isolated by filtration, washed with diethyl ether, and air-dried for about 2.5 weeks during which period its color changed to green. Anal. Calcd for $CuC_8H_8N_6O_6$: C, 27.63; H, 2.32; N, 24.17. Found: C, 27.44; H, 2.37; N, 24.15. Yield: 23%.

Single crystals of **1** for X-ray structural analysis were obtained by recrystallization of a sample prepared as above from acetonitrile. The product thus obtained consisted of green crystals of **1** intimately mixed with blue powder. The crystals were used in the X-ray studies while bulk studies on this compound were made on powdered samples prepared as outlined in the preceding paragraph.

(Nitrato)(nitrato-*O,O′*)tris(pyridazine)copper(II), $[Cu(pdz)_3(NO_3)_2]$, 2. Pyridazine (5.51 mmol) was slowly added to a filtered solution of copper(II) nitrate trihydrate (2.05 mmol) dissolved in 10 mL of ethanol containing 10% v/v 2,2-dmp. Less than the 3:1 ligand to metal mole ratio required by the stoichiometry of the complex was used in order to prevent the possible formation of a tetrakis(pyridazine) derivative. For the same reason, the pyridazine was added to the copper(II) solution rather than in the reverse order of addition. The blue precipitate was isolated by filtration, washed with a small amount of solvent, and dried for 1.5 h *in vacuo*. Anal. Calcd for $CuC_{12}H_{12}N_8O_6$: C, 33.69; H, 2.83; N, 26.19. Found: C, 33.63; H, 2.86; N, 26.28. Yield: 73%. On some occasions, repeats of the synthetic procedure did not result in immediate precipitation of a product. In these instances, the reaction vessel was covered with Parafilm and kept in a freezer (−5 °C) for several days whereupon X-ray quality crystals were obtained. The crystals were dried in a desiccator over drierite.

Table 1. Crystallographic Data[a,b]

compound	$[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**	$[Cu(pdz)_4(NO_3)][NO_3]$, **4**
formula	$C_{24}H_{24}Cu_3N_{18}O_{18}$	$C_{16}H_{16}CuN_{10}O_6$
fw	1043.20	507.91
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.938(1)	10.6425(9)
b, Å	13.6677(6)	16.442(1)
c, Å	14.933(2)	11.9930(6)
β, deg	96.03(1)	98.225(6)
Z	2	4
V, Å^3	1814.1(5)	2076.9(2)
ϱ_{calcd}, g cm^{-3}	1.910	1.624
$F(000)$	1050	1036
μ, cm^{-1}	29.34	19.67
radiation (λ, Å)	Cu Kα (1.541 78)	Cu Kα (1.541 78)
temp, °C	21	21
R	0.029	0.034
R_w	0.035	0.040

[a] Estimated standard deviations in the last digit are given in parentheses. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$.

Bis(nitrato)tetrakis(pyridazine)copper(II), $[Cu(pdz)_4(NO_3)_2]$, 3. A solution of copper(II) nitrate trihydrate (1.38 mmol) in 10 mL of ethanol containing 10% v/v 2,2-dmp was filtered into a flask containing pyridazine (8.26 mmol) and stirred briefly. The violet precipitate which formed was isolated by filtration, washed with a small amount of solvent and dried for 1 h *in vacuo*. Anal. Calcd for $CuC_{16}H_{16}N_{10}O_6$: C, 37.84; H, 3.18; N, 27.58. Found: C, 37.47; H, 3.07; N, 27.75. Yield: 54%.

(Nitrato)tetrakis(pyridazine)copper(II) nitrate, $[Cu(pdz)_4(NO_3)][NO_3]$, 4. This blue complex was prepared following the same procedure as described above for **3** using 2.04 mmol of copper(II) nitrate trihydrate and 8.26 mmol of pyridazine. Anal. Calcd for $CuC_{16}H_{16}N_{10}O_6$: C, 37.84; H, 3.18; N, 27.58. Found: C, 37.83; H, 3.23; N, 27.70. Yield: 57%. On one occasion, a repeat of the synthetic procedure did not result in an immediate precipitation of a product. However a blue crystalline precipitate formed immediately on application of a vacuum to the reaction mixture for a brief period. The mixture was left sitting for 2 days, and X-ray quality single crystals formed. These were isolated by decantation, washed with anhydrous diethyl ether and dried in a desiccator over Drierite for 1 day. During the latter procedure some of the crystals were observed to begin to darken. The crystal selected for the X-ray study, however, showed no visible sign of decomposition.

X-ray Crystallographic Analyses of $[Cu(pdz)_3(NO_3)_3]_2Cu$, 1, and $[Cu(pdz)_4(NO_3)][NO_3]$, 4. Crystallographic data for the two compounds appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 90.5-110.7°$ for **1** and 108.4−114.8° for **4**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for **1** and decayed uniformly by 3.3% for **4**. The data were processed[15] and corrected for Lorentz and polarization effects, decay (for **4**), and absorption (empirical, based on azimuthal scans for three reflections).

The structures were both solved by conventional heavy atom methods, the coordinates of the Cu atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The $[Cu(pdz)_3(NO_3)_3]_2Cu$ molecule, **1**, has exact (crystallographic) C_i symmetry. The terminal N(9) nitrate group in **1** is 2-fold orientationally disordered. The nitrogen atom could not be resolved but the oxygen atoms were refined as split atoms. A group occupancy factor was determined by constrained refinement of the population parameter with fixed (and equal) isotropic thermal parameters. In the final stages of refinement the occupancy factors were kept fixed.

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(15) TEXSAN/TEXRAY structure analysis package (Molecular Structure Corp., 1985).

Table 2. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**[a]

atom	*x*	*y*	*z*	B_{eq}	occ
Cu(1)	$^1/_2$	$^1/_2$	$^1/_2$	2.17(2)	
Cu(2)	0.30422(4)	0.28631(2)	0.49440(2)	2.56(1)	
O(1)	0.5193(2)	0.3464(1)	0.4497(1)	2.89(7)	
O(2)	0.7112(2)	0.3530(2)	0.3729(2)	4.8(1)	
O(3)	0.5719(2)	0.2239(1)	0.3671(2)	4.08(9)	
O(4)	0.2246(2)	0.2109(1)	0.3871(1)	3.60(8)	
O(5)	0.2851(3)	0.3220(2)	0.2915(1)	4.9(1)	
O(6)	0.2438(3)	0.1723(2)	0.2493(2)	5.8(1)	
O(7)	0.0804(7)	0.2297(5)	0.5695(4)	4.3(3)	0.54
O(7A)	0.049(1)	0.2476(6)	0.5305(5)	4.8(3)	0.46
O(8)	−0.049(2)	0.0970(7)	0.566(1)	12.0(7)	0.54
O(8A)	−0.074(1)	0.1118(8)	0.5205(9)	9.8(7)	0.46
O(9)	−0.1272(6)	0.2152(4)	0.4882(4)	6.6(3)	0.54
O(9A)	0.0257(9)	0.1588(5)	0.6431(4)	6.8(3)	0.46
N(1)	0.2773(2)	0.4963(1)	0.4501(1)	2.34(7)	
N(2)	0.1998(2)	0.4117(1)	0.4485(1)	2.51(8)	
N(3)	0.4460(2)	0.4372(1)	0.6189(1)	2.35(7)	
N(4)	0.3624(2)	0.3554(1)	0.6159(1)	2.46(8)	
N(5)	0.3912(3)	0.1622(1)	0.5472(1)	2.83(8)	
N(6)	0.5308(3)	0.1709(2)	0.5874(2)	3.8(1)	
N(7)	0.6038(2)	0.3061(1)	0.3952(2)	2.94(9)	
N(8)	0.2522(3)	0.2365(2)	0.3065(2)	3.7(1)	
N(9)	−0.0206(3)	0.1760(2)	0.5505(2)	4.9(1)	
C(1)	0.2114(3)	0.5761(2)	0.4150(2)	2.7(1)	
C(2)	0.0644(3)	0.5761(2)	0.3737(2)	3.1(1)	
C(3)	−0.0135(3)	0.4906(2)	0.3726(2)	3.4(1)	
C(4)	0.0588(3)	0.4095(2)	0.4117(2)	3.1(1)	
C(5)	0.4881(3)	0.4789(2)	0.6977(2)	2.8(1)	
C(6)	0.4516(3)	0.4414(2)	0.7791(2)	3.4(1)	
C(7)	0.3680(3)	0.3573(2)	0.7763(2)	3.4(1)	
C(8)	0.3246(3)	0.3169(2)	0.6920(2)	3.2(1)	
C(9)	0.3171(3)	0.0781(2)	0.5437(2)	3.6(1)	
C(10)	0.3797(4)	−0.0055(2)	0.5849(2)	4.4(1)	
C(11)	0.5196(5)	0.0010(2)	0.6273(2)	4.9(2)	
C(12)	0.5936(4)	0.0913(2)	0.6263(2)	5.0(2)	

[a] $B_{eq} = (8/3)\pi^2\sum\sum \mathbf{U}_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i{\cdot}\mathbf{a}_j)$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**[a,b]

Cu(1)−O(1)	2.243(2)	O(1)[c]−N(7)[d]	1.291(3)
Cu(1)−N(1)	2.052(2)	O(2)−N(7)[d]	1.229(3)
Cu(1)−N(3)	2.074(2)	O(3)−N(7)[d]	1.222(3)
Cu(2)−O(1)	2.255(2)	O(4)[c]−N(8)[e]	1.302(3)
Cu(2)−O(4)	1.974(2)	O(5)−N(8)[e]	1.231(3)
Cu(2)−O(7)	2.516(7)	O(6)−N(8)[e]	1.221(3)
Cu(2)−N(2)	2.036(2)	O(7)[c]−N(9)[f]	1.175(7)
Cu(2)−N(4)	2.063(2)	O(8)−N(9)[f]	1.14(1)
Cu(2)−N(5)	1.993(2)	O(9)−N(9)[f]	1.369(6)

O(1)−Cu(1)−O(1)*	180.0	O(4)−Cu(2)−N(5)	88.22(9)
O(1)−Cu(1)−N(1)	87.76(7)	O(7)−Cu(2)−N(2)	92.9(2)
O(1)−Cu(1)−N(1)*	92.24(7)	O(7)−Cu(2)−N(4)	83.5(1)
O(1)−Cu(1)−N(3)	86.12(7)	O(7)−Cu(2)−N(5)	81.8(2)
O(1)−Cu(1)−N(3)*	93.88(7)	N(2)−Cu(2)−N(4)	88.57(8)
N(1)−Cu(1)−N(1)*	180.0	N(2)−Cu(2)−N(5)	174.55(8)
N(1)−Cu(1)−N(3)	89.81(8)	N(4)−Cu(2)−N(5)	89.41(8)
N(1)−Cu(1)−N(3)*	90.19(8)	O(1)−N(7)−O(2)[d]	118.2(2)
N(3)−Cu(1)−N(3)*	180.0	O(1)−N(7)−O(3)[d]	118.5(2)
O(1)−Cu(2)−O(4)	101.29(8)	O(2)−N(7)−O(3)[d]	123.2(2)
O(1)−Cu(2)−O(7)	170.5(1)	O(4)−N(8)−O(5)[e]	119.7(2)
O(1)−Cu(2)−N(2)	88.21(7)	O(4)−N(8)−O(6)[e]	116.7(3)
O(1)−Cu(2)−N(4)	87.12(7)	O(5)−N(8)−O(6)[e]	123.6(3)
O(1)−Cu(2)−N(5)	96.74(8)	O(7)−N(9)−O(8)[f]	136.3(8)
O(4)−Cu(2)−O(7)	88.0(1)	O(7)−N(9)−O(9)[f]	112.4(4)
O(4)−Cu(2)−N(2)	93.04(8)	O(8)−N(9)−O(9)[f]	111.0(7)
O(4)−Cu(2)−N(4)	171.47(8)		

[a] Standard deviations in the last digit are given in parentheses. [b] Asterisk refers to the following symmetry operation: $1-x$, $1-y$, $1-z$. [c] Coordinated to copper ion. [d] Involving monodentate bridging nitrate group. [e] Involving strongly coordinated terminal nitrate group. [f] Involving weakly coordinated terminal nitrate group.

Table 4. Final Atomic coordinates (fractional) and B_{eq} (Å^2) for $[Cu(pdz)_4(NO_3)][NO_3]$, **4**[a]

atom	*x*	*y*	*z*	B_{eq}
Cu(1)	0.19308(3)	0.52656(2)	0.22467(2)	2.86(1)
O(1)	0.2639(2)	0.6050(1)	0.3706(1)	4.06(7)
O(2)	0.2756(2)	0.7121(1)	0.2681(2)	5.2(1)
O(3)	0.2625(2)	0.7246(1)	0.4437(2)	5.7(1)
O(4)	0.6121(3)	0.6197(2)	0.2697(2)	7.8(1)
O(5)	0.7076(3)	0.6601(2)	0.4274(2)	8.3(2)
O(6)	0.7239(4)	0.5390(2)	0.3721(3)	11.3(2)
N(1)	0.0708(2)	0.4567(1)	0.2956(1)	2.96(7)
N(2)	−0.0156(2)	0.4201(1)	0.2198(2)	3.79(9)
N(3)	0.2882(2)	0.5521(1)	0.0947(2)	3.20(7)
N(4)	0.2472(2)	0.5028(2)	0.0082(2)	4.4(1)
N(5)	0.3309(2)	0.4448(1)	0.2798(2)	3.15(7)
N(6)	0.3129(2)	0.3721(1)	0.2305(2)	4.7(1)
N(7)	0.0485(2)	0.6014(1)	0.1657(1)	3.03(7)
N(8)	−0.0042(2)	0.6386(1)	0.2469(2)	3.90(9)
N(9)	0.2679(2)	0.6818(1)	0.3604(2)	3.47(8)
N(10)	0.6777(3)	0.6069(2)	0.3593(2)	5.3(1)
C(1)	0.0752(3)	0.4433(2)	0.4046(2)	3.6(1)
C(2)	−0.0115(3)	0.3922(2)	0.4458(2)	4.3(1)
C(3)	−0.0994(3)	0.3552(2)	0.3706(3)	4.5(1)
C(4)	−0.0966(3)	0.3702(2)	0.2581(3)	4.3(1)
C(5)	0.3789(3)	0.6051(2)	0.0892(2)	4.1(1)
C(6)	0.4362(3)	0.6132(2)	−0.0079(3)	5.5(2)
C(7)	0.3965(4)	0.5636(2)	−0.0956(3)	5.6(2)
C(8)	0.3012(3)	0.5092(2)	−0.0838(2)	5.2(1)
C(9)	0.4315(3)	0.4592(2)	0.3546(2)	4.0(1)
C(10)	0.5225(3)	0.3999(2)	0.3874(2)	4.7(1)
C(11)	0.5053(3)	0.3265(2)	0.3385(3)	4.8(1)
C(12)	0.3997(3)	0.3153(2)	0.2591(3)	5.3(1)
C(13)	0.0045(3)	0.6147(2)	0.0583(2)	3.6(1)
C(14)	−0.0954(3)	0.6669(2)	0.0245(2)	4.4(1)
C(15)	−0.1476(3)	0.7067(2)	0.1056(3)	4.3(1)
C(16)	−0.0992(3)	0.6894(2)	0.2165(2)	4.3(1)

[a] $B_{eq} = (8/3)\pi^2\sum\sum \mathbf{U}_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i{\cdot}\mathbf{a}_j)$.

All non-hydrogen atoms of both structures were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (O−H/C−H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Secondary extinction corrections were applied in both cases, the final values of the extinction coefficient being $1.81(4) \times 10^{-6}$ and $3.44(5) \times 10^{-6}$, respectively for **1** and **4**. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 16. Final atomic coordinates and equivalent isotropic thermal parameters, and selected bond lengths and bond angles appear in Tables 2−5. Complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for both structures are included as supplementary material.

Physical Measurements. Infrared spectra in the range 4000−250 cm^{-1} were recorded on a Perkin-Elmer Model 598 spectrometer using samples mulled in Nujol or hexachlorobutadiene and pressed between KRS-5 plates (Harshaw Chemical Co.). Calibration was achieved using polystyrene, and band frequencies are considered accurate to ±3 cm^{-1}. Electronic spectra in the 25000−5000 cm^{-1} range were recorded on a Cary 5 UV−vis−near-IR spectrophotometer. Samples were mulled in Nujol and sandwiched between quartz glass plates. A second set of plates containing only Nujol was placed in the reference beam. EPR spectra on powder samples at liquid nitrogen temperature were recorded on a Varian Associates E3 spectrometer using 100 kHz field modulation. The X-band microwave frequency was monitored on a Hewlett-Packard 5245L electronic counter equipped with a 3−12.4 GHz frequency converter. Magnetic susceptibilities for $[Cu(pdz)_3(NO_3)_3]_2Cu$ over the range 4.2−345 K and at a field of 10 000 Oe were measured using a Quantum Design (MPMS) SQUID magnetometer. The sample holder, possessing a constant cross-sectional area, was made from PVC. For the remainder of the complexes, magnetic susceptibilities over the temperature range ~4.2−82 K were measured at an applied field of 9225 Oe using a PAR Model 155 vibrating sample magnetometer as

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(16) *International Tables for X-Ray Crystallography*, Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99−102 and 149.

Table 5. Selected bond lengths (Å) and angles (deg) for $[Cu(pdz)_4(NO_3)][NO_3]$, **4**[a]

Cu(1)−O(1)	2.217(2)	O(5)−N(10)[c]	1.208(3)
Cu(1)−N(1)	2.014(2)	O(6)−N(10)[c]	1.221(4)
Cu(1)−N(3)	2.021(2)	N(1)−N(2)	1.339(3)
Cu(1)−N(5)	2.029(5)	N(1)−C(1)	1.320(3)
Cu(1)−N(7)	2.018(2)	N(2)−C(4)	1.320(3)
O(1)[b]−N(9)	1.270(3)	C(1)−C(2)	1.390(4)
O(2)−N(9)	1.228(3)	C(2)−C(3)	1.348(4)
O(3)−N(9)	1.231(3)	C(3)−C(4)	1.376(4)
O(4)−N(10)[c]	1.213(3)		
O(1)−Cu(1)−N(1)	99.54(7)	O(1)−N(9)−O(3)	119.0(2)
O(1)−Cu(1)−N(3)	109.68(8)	O(2)−N(9)−O(3)	122.4(3)
O(1)−Cu(1)−N(5)	88.82(7)	O(4)−N(10)−O(5)[c]	122.4(3)
O(1)−Cu(1)−N(7)	94.47(7)	O(4)−N(10)−O(6)[c]	116.1(3)
N(1)−Cu(1)−N(3)	150.46(8)	O(5)−N(10)−O(6)[c]	121.0(3)
N(1)−Cu(1)−N(5)	88.00(8)	N(1)−C(1)−C(2)	121.4(2)
N(1)−Cu(1)−N(7)	89.39(7)	C(1)−C(2)−C(3)	117.9(2)
N(3)−Cu(1)−N(5)	88.33(8)	C(2)−C(3)−C(4)	117.7(3)
N(3)−Cu(1)−N(7)	92.52(8)	N(2)−C(4)−C(3)	124.0(3)
N(5)−Cu(1)−N(7)	176.10(8)	N(2)−N(1)−C(1)	121.4(2)
O(1)−N(9)−O(2)	119.9(2)	N(1)−N(2)−C(4)	117.5(2)

[a] Standard deviations in the last digit are given in parentheses. [b] Coordinated to copper ion. [c] Involving ionic nitrate group.

previously described.[17] Samples were held in Kel-F capsules. Susceptibility measurements at 7501 Oe gave no evidence for field dependent susceptibilities. Magnetic susceptibilities were corrected for diamagnetism of all atoms (Cu^{2+}, −11; pdz, −45; NO_3^-, −20) and temperature independent paramagnetism of Cu^{2+}, 60. All corrections are in units of 10^{-6} cm^3 mol^{-1}. Carbon, hydrogen, and nitrogen analyses were performed by P. Borda of this department.

Results and Discussion

Structures of the Complexes. This work aims at further characterizing the coordination behaviour of pyridazine and investigating how magnetic properties correlate with structure, particularly where bridging pyridazine ligands are involved. Fortunately three of the four compounds characterized here were obtained in crystalline form suitable for single-crystal X-ray diffraction studies.

The structure of $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1** with the atom numbering scheme is shown in Figure 1 and the crystal packing diagram is given in Figure 2. The latter shows that both intra- and inter-molecular hydrogen-bonding (H-bonding), involving the hydrogen atoms of the pyridazine and the oxygen atoms of the nitrate groups, exist in this compound. This complex has a centrosymmetric linear trimetallic structure. The copper ions are linked by two bidentate bridging pyridazine groups and one monodentate bridging nitrate group. The central copper ion is thus surrounded by four pyridazine and two nitrate groups. Octahedral coordination around each of the terminal copper ions is completed by one monodentate pyridazine ligand and two monodentate terminal nitrate groups.

There are three distinct types of nitrate groups distinguished by the mode or strength of coordination to the metal. These are monodentate bridging, strongly coordinated monodentate terminal, and weakly coordinated monodentate terminal. Examples of complexes in which a single oxygen atom of the nitrate group bridges two metals as seen in **1** are rare, although this bridging mode has previously been observed.[4,18] However, while the Cu−O−Cu bridges are essentially symmetrical in **1**, they are asymmetrical in the complexes previously studied. The dimensions of the strongly coordinated monodentate terminal nitrate group, along with those of the monodentate bridging one,

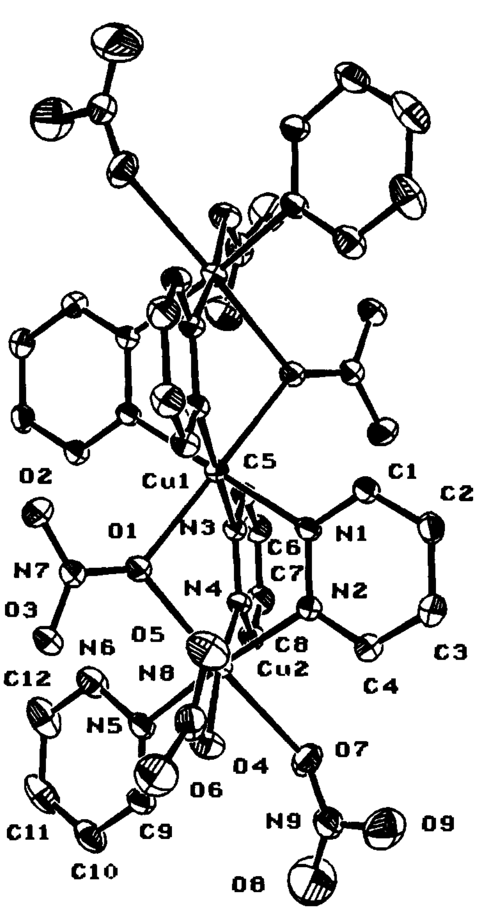

Figure 1. The structure of $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**, with atom numbering scheme. The 33% probability thermal ellipsoids are shown. Hydrogen atoms and minor disordered component of the N(9) nitrate group have been omitted for clarity.

are similar to those that have been observed in other complexes containing monodentate nitrate groups.[19] The N−O bond lengths involving the coordinated oxygen atoms are the longest and fall within the range 1.26−1.32 Å whereas the terminal N−O bond lengths lie in the range 1.21−1.24 Å. The third type of the nitrate group in **1** is characterized by a considerably longer Cu−O bond length, a probable consequence of steric factors. This nitrate group is disordered and some unexpected dimensions observed for it (Table 3) are most certainly a consequence of the disorder.

Both the central and terminal copper ions in **1** have elongated tetragonal octahedral geometries. However, the former has a CuN_4O_2 chromophore with a 4 + 2 type coordination whereas the latter have $CuN_3OO'O''$ chromophores with (1 + 4 + 1) type coordination, one of the Cu−O bond lengths being comparable to the three Cu−N bond lengths. In the chromophores of the terminal copper ions, the Cu−N bond involving the terminal pyridazine ligand is slightly shorter than those involving the bridging ones. This is probably an electronic effect. In a bridging pyridazine ligand coordination through one nitrogen may effectively reduce the donor ability of the neighbouring nitrogen such that overall weaker bonds to the metal are formed than if the ligand is bonded through one nitrogen only. Regarding Cu−O distances, it is interesting to note that one of the Cu−O distances involving a terminal nitrate group is shorter while the other is longer than those involving the bridging nitrate groups. As mentioned in the preceding paragraph the considerably longer Cu−O bond of 2.516(7) Å is probably a consequence of steric constraints.

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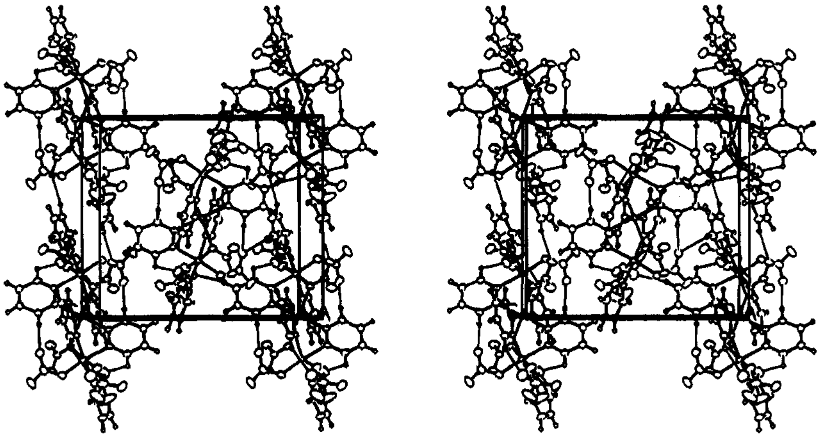

Figure 2. Stereoview of the unit cell packing diagram for $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**.

All the pyridazine rings in **1** are planar within experimental error and their internal bonding parameters are comparable to those observed in **4** (Table 5) and to other published data.[20,21] Both bidentate bridging and monodentate terminal pyridazine ligands are present, and to our knowledge, this is the first X-ray structure determination to be reported on a compound with both pyridazine bonding modes. In addition, of the four compounds isolated in this work, this is the only one to contain bridging pyridazines. Since the only complex reported for the corresponding pyrazine system is the extended linear chain, pyrazine-bridged compound $Cu(pyz)(NO_3)_2$, it would appear that, at least in these systems, pyridazine has a greater tendency to bond in a monodentate fashion than does pyrazine.

$[Cu(pdz)_3(NO_3)_2]$, **2**, is a monometallic complex with a distorted octahedral geometry.[14] The copper coordination sphere consists of three monodentate pyridazine ligands, one monodentate nitrate group, and one asymmetrically chelating nitrate group.

$[Cu(pdz)_4(NO_3)_2]$, **3**, was not isolated in a form suitable for an X-ray structural determination, and on the basis of spectroscopic studies described below, we propose for it a monometallic *trans*-octahedral structure in which all the ligands are monodentate.

The structure of $[Cu(pdz)_4(NO_3)][NO_3]$, **4**, with the atom numbering scheme is shown in Figure 3. The compound has an ionic structure with both coordinated and ionic nitrate groups. The complex cation is irregular five-coordinate with four monodentate pyridazine groups and one monodentate nitrate. The internal bonding parameters of the coordinated nitrate group in this compound (Table 5) are in good agreement with those reported in the literature for similarly bonded nitrates.[19] The N−O bond distances of the non-coordinated nitrate ion are all approximately equal (average = 1.214 Å) and compare favorably with values previously reported for transition metal complexes containing ionic nitrate groups.[22] All the pyridazine rings in **4** are planar within experimental error. There is extensive H-bonding in **4** as seen in the unit cell packing diagram shown in Figure 4. The coordinated nitrate group is involved in intramolecular H-bonds with pyridazine ligands. In addition, all three oxygen atoms of the noncoordinated nitrate ion are H-bonded, but each to a pyridazine ligand bonded to a different copper ion thereby linking the various molecular units into a three-dimensional network.

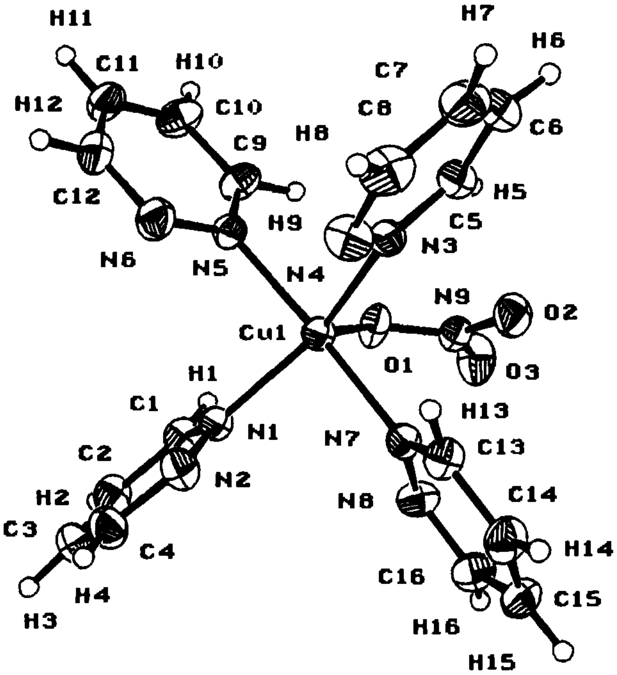

Figure 3. The structure of the $[Cu(pdz)_4(NO_3)]^+$ cation with atom numbering scheme. The 33% probability thermal ellipsoids are shown.

Spectroscopic Studies. Interest in spectroscopically characterizing the complexes studied here was generated, in part, from the fact that such information obtained on compounds of known structure, such as **1**, **2**, and **4**, can often be used to obtain indirect structural information on microcrystalline compounds, as is done here for **3**. Bands observed in the infrared spectra of the complexes were tentatively assigned to nitrate group vibrations by comparison of the spectra with those of free pyridazine[23] and other complexes containing pyridazine[24] or nitrate[25,26] groups. Data and assignments[27] are given in Table 6. The spectrum of **3** most closely resembles that of **4** with the main difference being the presence of an additional band at $1371 cm^{-1}$. A possible explanation of these observations is that in **3** while one nitrate is fully coordinated as in **4**, the second nitrate rather than occupying a "free" lattice position as in **4** is weakly coordinated to the metal. This form of coordination, previously termed semicoordination,[28] can lead to small distortions of the anion and an infrared spectrum intermediate between

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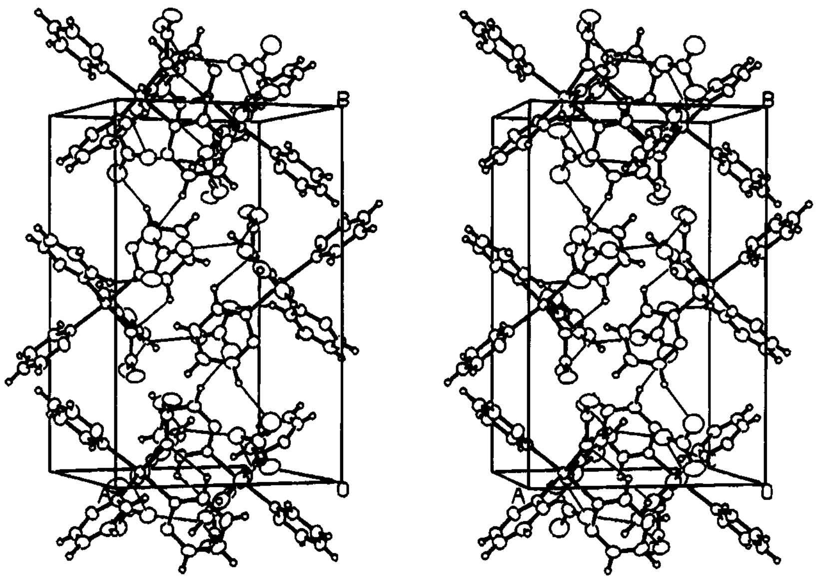

Figure 4. Stereoview of the unit cell packing diagram for $[Cu(pdz)_4(NO_3)][NO_3]$, **4**.

Table 6. Selected Spectral Data for Pyridazine Complexes of Copper(II) Nitrate[a,b]

		1	**2**	**3**	**4**
		Infrared Spectra (Nitrate Bands)[c]			
ν_3(E′)	1390	1478 s, br	1465 s		
		1399 s[d]	1402 s[d]	1410 s[d]	1406 s[d]
				1371 s	
		1328 s	1322 s	1342 s	1345 s
		1286 s br	1301 s	1314 s	1311 s
ν_1(A_1′)	1050	1041 m	1039 m	1039 s	1037 s
		1025 s	1018 s		
ν_2(A_2″)	831	829 m	826 s	831 m	831 w
		810 m	816 s	823 w−m	822 m
ν_4(E′)	720	744 m	744 s	746 s	746 s
		722 m		717 w	718 m
		Electronic Spectra (Band Maxima)			
		15 500	15 400	17 500	15 900
		EPR Spectra[e,f]			
g_1		2.292	~2.24	2.216	2.235
g_2		2.060	2.083	2.065	2.080
g_3		2.011			2.048
g_0		2.121	~2.14	2.115	2.121

[a] All infrared and electronic spectral data are in cm^{-1}. Key: s = strong, m = medium, w = weak, br = broad. [b] **1** = $[Cu(pdz)_3(NO_3)_3]_2Cu$, **2** = $[Cu(pdz)_3(NO_3)_2]$, **3** = $[Cu(pdz)_4(NO_3)_2]$, **4** = $[Cu(pdz)_4(NO_3)][NO_3]$. [c] The first two columns are band assignments and frequencies for free nitrate (data and assignment, D_{3h} symmetry, from ref 27). [d] Pyridazine also absorbs in this region. [e] Estimated error in g values = ±0.003. When only two g values are observed $g_1 = g_{\parallel}$ and $g_2 = g_{\perp}$. g_0 = isotropic g value and is calculated as follows: $g_0 = (g_1 + g_2 + g_3)/3$ for **1** and **4** and $g_0 = (g_{\parallel} + 2g_{\perp})/3$ for **2** and **3**. [f] There is evidence of a weak signal ($g \sim 2.11$) of unknown origin in the EPR spectrum of **3**.

that of the free ion and the fully-coordinated ion.[29] The effect of weak anion coordination in this case is seen in the splitting of ν_3 (E′) into bands at 1410 and 1371 cm^{-1}.

The electronic spectra of the four complexes each consist of a single broad band in the visible region with the band maximum in **3** significantly higher in energy than those observed for **1**, **2** and **4** (Table 6). This probably reflects a highly tetragonal CuN_4O_2 chromophore for this compound. In support of this is the fact that pyridine complexes of the type *trans*-$Cu(py)_4X_2$, where X is a weakly coordinating anion, typically exhibit broad single-band electronic spectra with maxima near or above 17 000 cm^{-1}. The electronic absorption band maximum in *trans*-$[Cu(py)_4(CF_3SO_3)_2]$, for example, is 17 400 cm^{-1}.[30] A structure involving axially coordinated nitrate groups for **3** is also supported by the epr spectrum of the compound as discussed below.

Values of g obtained from the EPR spectra are given in Table 6. The spectrum of **1** may be interpreted as a rhombic spectrum in which the two metal sites (central and terminal) are not distinguishable or as a composite of two axial spectra in which the perpendicular components partially overlap and the parallel components are unresolved. Although the structure of **2**[14] reveals the metal to have a ligand environment of lower than axial symmetry, a three g-value spectrum is not seen for this compound. Nonetheless, although the spectrum appears axial; the bands are broad, and $g_{\parallel}$ is not well resolved. The three g-value spectrum observed for **4** is consistent with the known structure involving a lower than axial ligand environment about the metal. The axial spectrum observed for **3** supports a tetragonally distorted octahedral structure for this compound. In summary, the infrared, visible, and EPR studies are all consistent with a monometallic structure for **3** with four monodentate pyridazines and two monodentate nitrates, the latter occupying *trans* positions in a CuN_4O_2 chromophore.

Magnetic Properties Magnetic susceptibility and magnetic moment data at various temperatures have been deposited as supplementary material. Freshly prepared samples of **2**, **3**, and **4** exhibit temperature invariant magnetic moments of 1.83, 1.79, and 1.83 μ_B, respectively, in the range 82−4.3 K. Employing the expression $\mu_{eff} = g_0[S(S + 1)]^{1/2}$ to calculate magnetic moments from EPR measured values of g_o (Table 6) we obtain values of 1.85, 1.83, and 1.84 μ_B, respectively,for these compounds, in good agreement with the values obtained from magnetic susceptibility measurements. This result, together with the observation that the magnetic moments are temperature independent over the temperature range studied, shows these compounds to be magnetically dilute.[30] This is consistent with the monomeric structures determined by X-ray crystallography for **2**[14] and **4** and proposed on the basis of indirect evidence for

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3. Compound **1** has a magnetic moment of 1.52 μ_B per copper ion at 345 K. This is significantly less than the value of 1.84 μ_B calculated from the EPR determined g_o value. This result together with the observation that the magnetic moment decreases gradually to a value of 1.20 μ_B at 90 K, and then remains constant as the temperature is further lowered to 4.2 K, indicates a spin doublet ground state and strong antiferromagnetic coupling between the metal centers.

The magnetic susceptibility of a symmetrical linear copper(II) trimetallic complex is given by the expression[31,32]

$$\chi_{tri} = \frac{Ng^2\beta^2}{4kT}\left(\frac{e^{-2J/kT} + e^{-2J'/kT} + 10e^{J/kT}}{e^{-2J/kT} + e^{-2J'/kT} + 2e^{J/kT}}\right)$$

where J is the exchange constant between the central and terminal copper ions and J' is the exchange constant between the terminal copper ions. The other symbols have their usual meanings. Experimental reciprocal susceptibilities of **1** were analyzed by this expression. Setting J' equal to zero and treating J and g as the variable parameters gave a good fit with $J = -170 \text{cm}^{-1}$ $g = 2.40$, and $F = 0.0167$.[33] The value of g, however, is considered unrealistically high, particularly in view of the EPR results discussed above. Fixing g at the $g_o = 2.12$ obtained from the EPR experiment did not yield a good fit to the data ($J = -99$ cm^{-1}, $F = 0.1592$). A much improved fit was obtained when all three parameters, J, J', and g, were varied ($F = 0.0084$). However, this procedure also gave an unrealistically high value of g (2.39) and, in addition, both J and J' were indeterminate. Consequently, the susceptibility data were analyzed assuming the presence of a paramagnetic component, P.[34] J and P were treated as adjustable parameters, with J' and g held at 0 and 2.12, respectively. Excellent agreement between experiment (34 fitted data points) and theory was obtained with $J = -139$ cm^{-1}, $P = 0.135$, and $F = 0.0087$ (Figure 5). While the paramagnetic component could consist of small amounts of the other complexes characterized here, the analytical data do not support levels beyond ~5% of these compounds. It seems more likely that this component is an isomer of **1**, for example, a monometallic form of [Cu(pdz)$_2$(NO$_3$)$_2$] in which the pyridazines are monodentate and the nitrates are bidentate chelating.

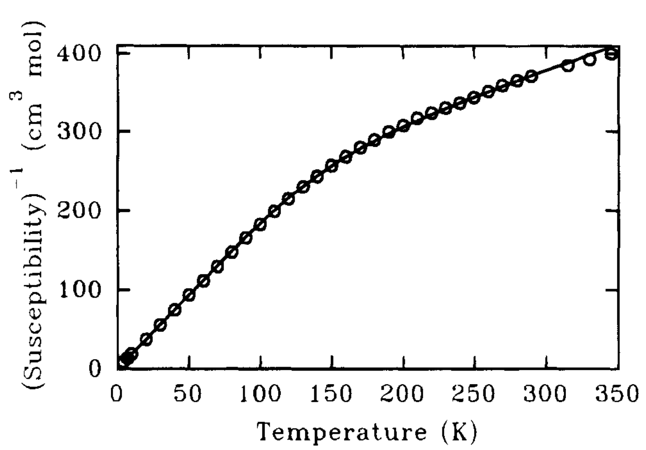

Figure 5. Plot of reciprocal susceptibility (34 fitted data points) versus temperature for [Cu(pdz)$_3$(NO$_3$)$_3$]$_2$Cu, **1**. Solid line was generated with $J = -139$ cm^{-1} and $g = 2.12$, and $P = 0.135$.

In an attempt to place the magnitude of exchange coupling in **1** ($J = -139$ cm^{-1}) in perspective, we searched the literature for magnetic studies on related compounds. Comparisons with pyrazine complexes shows the coupling in **1** to be significantly larger than that observed for Cu(pyz)(NO$_3$)$_2$[10,11] and, indeed, for any copper(II) pyrazine complex studied to date.[2] Comparisons with other complexes containing copper(II) bridged by the 1,2-diazine link are also of interest. Although there are many examples of trimetallic complexes of copper(II) which have been characterized by both single crystal X-ray diffraction and variable temperature magnetic susceptibility studies,[31,32,35–41] none have bridging pyridazines, and most have bridging oxygens derived from a variety of different ligands. Most however, like **1**, show strong antiferromagnetism and a spin doublet ground state. Trimetallic structures have also been proposed for other copper(II) complexes but these have not been confirmed by single crystal X-ray diffraction studies.[32,37,41–44] Of particular relevance to the present work is [Cu(bpdpn)]$_2$CuCl$_2$, where H$_2$-bpdpn is *N,N'*-bis(3'-pyridazinecarboxamide)-1,3-propane.[44] A trimetallic structure in which only the substituted pyridazines act as bridging ligands has been proposed for this compound. Its magnetic moment per copper ion, reported for two temperatures only, is 1.55 μ_B at 304 K and 1.10 μ_B at 89 K. Although no detailed analysis of the magnetic data was presented, the magnitude of the magnetic moment at the two temperatures is comparable to those obtained for **1** indicating the exchange in the two compounds is approximately the same strength. This would be consistent with equivalent exchange pathways in the two complexes involving the 1,2-diazine linkages of the pyridazine derivatives in the chloro complex and the pyridazine bridges in **1**. The bridging nitrates in **1** are, in fact, unlikely to be involved in a significant way in mediating exchange since they occupy the long-bonded positions in the copper coordination spheres. There have been several studies on dimetallic complexes containing substituted pyridazine ligands and having structures involving 1,2-diazine links. These complexes have J values ranging from 65 to 652 cm^{-1},[4–6] thus spanning the value observed for **1**. Further comparisons are made difficult by the fact the dimetallic complexes also contain chloro, bromo, or hydroxo bridges. Perhaps the most significant comparison

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(33) In the least-squares fitting procedure employed the following is the function minimized:

$$F = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\chi^i_{calc} - \chi^i_{obs}}{\chi^i_{obs}}\right)^2\right]^{1/2}$$

where n is the number of data points and χ^i_{obs} and χ^i_{calc} are the experimental and calculated molar magnetic susceptibilities. The F value gives a measure of the quality of the fit between experiment and theory.

(34) To allow for the paramagnetic component the calculated susceptibility, χ_{calc}, is obtained by combining the theoretical susceptibility for the trimetallic model, χ_{tri}, with the Weiss term, $\chi_{para} = Ng^2\mu_B^2S(S+1)/kT$, in the following way:

$$\chi_{calc} = (1 - P)\chi_{tri} + P\chi_{para}$$

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is with the pyridazine complexes, $Cu(pdz)X_2$ = (X = Cl, Br, or NCO), which are all thought to have structures involving chains of copper ions singly bridged by pyridazines. The values of J measured for these compounds are in the range -32 to -44 cm^{-1}.[2,7,8] The fact the exchange in **1** is over three times that in these complexes probably reflects, in part at least, the differences in the number of pyridazines bridging the metal centers.

Decomposition Reactions of 2, 3, and 4. As described in the experimental section, compounds **2**, **3**, and **4** show visible signs of decomposition over time. In an effort to determine what is taking place during the decomposition we examined a sample of $[Cu(pdz)_4(NO_3)_2]$, **3**, which, within 2 weeks and while sealed in a vial and kept in a nitrogen atmosphere glovebox, had changed from its original violet color to black. Elemental analysis revealed no change from the original values while magnetic susceptibility measurements showed the magnetic moment to have dropped to a temperature independent value (82–4.2 K) of about 1.2 μ_B. This magnetic behavior is very similar to that observed for the trimetallic species, **1**. It thus appears that on standing **3** undergoes a structural rearrangement in the solid state to form **1**. This requires the release of six pyridazine molecules for every trimetallic species formed. The black complex is therefore formulated as $[Cu(pdz)_3(NO_3)_3]_2Cu\cdot 6dpz$. Pyridazine is a light orange liquid but discolors when irradiated,[45] thus accounting for the color changes. Similar tests on decomposed samples of **2** indicate similar though less dramatic results. A sample which had changed color from bright blue to greenish blue was found to have unchanged microanalytical data but a decreased magnetic moment (from 1.83 to 1.70 μ_B). The color of **4** was also observed to change from blue to black on standing. No magnetic studies of the black product were undertaken in this case. Since the decompositions described here resulted in loss of crystallinity and since repeated attempts to obtain interpretable spectroscopic data on the decomposition products were unsuccessful, further speculation about the processes taking place is not warranted at this time.

Summary and Conclusions

A systematic study of the products of the reaction of pyridazine with copper(II) nitrate in ethanol revealed conditions for obtaining four distinct products and although one of them, $[Cu(pdz)_3(NO_3)_3]_2Cu$, **1**, contains both bridging and terminal pyridazine ligands, the other three, $[Cu(pdz)_3(NO_3)_2]$, **2**, $[Cu(pdz)_4(NO_3)_2]$, **3**, and $[Cu(pdz)_4(NO_3)][NO_3]$, **4**, contain only terminal ligands. No evidence for a pyridazine analogue of the extended chain pyrazine complex, $Cu(pyz)(NO_3)_2$ was obtained; in fact, no polymeric structures of any type seem to be present in this system. Hence, the presence of monodentate pyridazine dominates the coordination chemistry of this ligand in this system and the tendency of pyridazine to bridge metal centers, at least in the presence of weakly coordinating anions, appears to be significantly less than that of pyrazine. It is interesting to note that, in the early work on pyrazine complexes,[46] it was thought that coordination by one nitrogen of that ligand would sufficiently lower the basicity of the other that there would be little tendency to bridge. It appears that this effect is more pronounced in the case of pyridazine where the nitrogens are adjacent. Experimental evidence for this effect is also seen in the structures of **1**, **2**, and **4** in which the Cu–N bonds for the terminal pyridazines are, on average, shorter than those of the bridging pyridazines in **1**.

The novel trimetallic complex, **1**, provides the first example of a structurally and magnetically characterized complex in which both terminal and bridging pyridazines are present and in which the metals are doubly bridged by pyridazine. This form of bridging is, of course, not possible for the linear bridging pyrazine. Although bulk samples of **1** required for the magnetic measurements were determined to contain a paramagnetic component assigned to a structural isomer, analysis of the magnetic susceptibility data, employing the EPR-determined g value, permitted the determination of $J = -139$ cm^{-1} for **1**. The magnitude of this exchange coupling is much greater than that seen in any complex of pyrazine, supporting the earlier conclusion[2] that the two atom pathway provided by pyridazine is significantly more efficient at mediating magnetic exchange. The result also indicates that two bridging pyridazines are more efficient than one as the exchange in **1** is more than three times stronger than that observed in the singly bridged $Cu(pdz)X_2$ complexes. This conclusion relies on the assumption that the nitrates are not contributing significantly to the exchange pathway in **1**, an assumption that seems reasonable since the bridging nitrates occupy the long- bonded positions in the copper coordination spheres in **1**.

While **1** appears to be indefinitely stable, compounds **2**, **3**, and **4** showed visible signs of decomposition over time. This was interpreted in terms of molecular rearrangements in the solid state involving, possibly, changes in pyridazine coordination yielding complex **1** and conversion of some coordinated pyridazine to lattice pyridazine.

Finally, the structures described here nicely illustrate the variety of bonding modes the nitrate ion can exhibit in coordination complexes. As discussed previously,[14] compound **2** contains both monodentate and chelating nitrates while, as described here, **4** contains ionic and monodentate nitrate and **1** contains three different types of nitrate: weakly and strongly coordinating monodentate nitrates and a rare form of nitrate coordination involving bridging by one oxygen atom.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Supplementary Material Available: Tables giving magnetic data for all compounds and crystal data and details of the structure determinations, hydrogen atom coordinates, bond lengths and angles, anisotropic thermal parameters, torsion angles, intermolecular contacts and least squares planes for $[Cu(pdz)_3(NO_3)_3]_2Cu$ and $[Cu(pdz)_4(NO_3)][NO_3]$ (42 pages). Ordering information is given on any current masthead page.

IC9407095

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