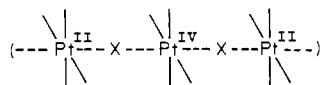recently applied by Whangbo[22] to Wolffram's red salt

can, with minor variations, be used to understand the electronic and structural properties of $Pt_2(CH_3CS_2)_4I$. In our compound the interaction can be considered to arise from dimers containing Pt(II) and dimers containing Pt(III), through bridged iodine. The two d_{z^2} bands are generated by σ^* in $Pt_2(CH_3CS_2)_4$, a doubly occupied orbital, and the same one in $Pt_2(CH_3CS_2)_4I_2$, a σ^* empty orbital, with a small energy gap, E_g. The near-IR absorption band can be reasonably assigned as arising from the transitions between these two bands. The temperature dependence of the electrical conductivity gives a very small apparent activation energy, 0.05 eV, which cannot be related to the near-IR band, ~ 1 eV, and therefore the intrinsic band mechanism should be excluded.[23] The electrical conduction then may occur either by an intrinsic "hopping mechanism"[24] or by an extrinsic band-model mechanism. The former seems the more appropriate to describe the conduction

in our complex. In fact, if we compare our results with those found by Interrante and co-workers[24] on $M(NH_3)_2X_3$ complexes, where M = Pd, Pt and X = halogen, we can reasonably suggest this process. In this series of compounds the conductivity is enhanced by pressure and reaches a maximum value as M(II)---X and M(IV)---X distances tend to become equal. The values of the conductivity and the activation parameter at high pressure are comparable with the values reported here, where the Pt–I distances are nearly equal. The EPR signal present in $Pt_2(CH_3CS_2)_4I$ could be explained as arising from crystal defects or "impurity centers" with an odd number of electrons along the chain. It is not yet possible to assess their contribution to the electrical conductivity from the data available. Further measurements are needed to elucidate the point.

Acknowledgment. We thank Mr. G. Cossu for ESCA measurements, Mr. M. Viola for the assembling of the apparatus for electrical conductivity measurements, Dr. D. Attanasio for helpful discussions, and finally one of the reviewers for his helpful comments.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and Louisiana State University, Baton Rouge, Louisiana 70803

Synthesis, Molecular Structure, and Magnetic Properties of Some Copper(II) Complexes of Bis(2-pyridylmethyl) Ketazine[1]

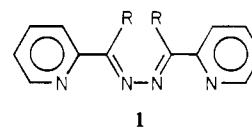CHARLES J. O'CONNOR,*[2a] RUDOLFO J. ROMANANCH,[2a] DANIEL M. ROBERTSON,[2a] ETIM E. EDUOK,[2a] and FRANK R. FRONCZEK[2b]

Two copper(II) complexes of the binucleating ligand bis(2-pyridylmethyl) ketazine (pmk) are reported. The two complexes crystallize with different stereoisomers of the pmk ligand. As a pure solid and in solution the pmk ligand exists as the trans, trans isomer. In the presence of $Cu(NO_3)_2$, pmk forms a soluble complex, which undergoes a template rearrangement yielding crystals of $Cu(cis,trans$-pmk$)(NO_3)_2$. When pmk is dissolved with $CuCl_2$, an insoluble binuclear complex forms without rearrangement of the ligand. The product of $CuCl_2$ and pmk has the formula $Cu_2(trans,trans$-pmk$)Cl_4$. The magnetic data show very weak antiferromagnetic interactions between the $Cu(cis,trans$-pmk$)(NO_3)_2$ monomeric units ($g = 2.22$, $\theta = -1.2$ K). The binuclear complex shows antiferromagnetic intradimer exchange ($g = 2.10$, $2J = -52$ cm^{-1}). Crystal data: $CuC_{14}H_{14}N_6O_6$, $M_r = 425.8$, space group $C2/c$, $a = 11.356$ (4) Å, $b = 17.325$ (5) Å, $c = 8.829$ (2) Å, $\beta = 91.61$ (3)°, $Z = 4$, $d_{calcd} = 1.629$ g cm^{-3}, μ(Mo Kα) = 13.6 cm^{-1}, $R = 0.079$ for 1534 reflections; $Cu_2Cl_4C_{14}H_{14}N_4$, $M_r = 507.2$, space group $P2_1/n$, $a = 9.058$ (2) Å, $b = 14.115$ (3) Å, $c = 14.892$ (3) Å, $\beta = 106.26$ (2)°, $Z = 4$, $d_{calcd} = 1.843$ g cm^{-3}, μ(Cu Kα) = 83.15 cm^{-1}, $R = 0.055$ for 1911 reflections.

Introduction

Binuclear metal(II) complexes of azine ligands have been known for several years.[3–12] Complexes of bis(2-pyridy)

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ketazine ligands (1, R = H) with the formula $M_2L_3X_4$ were

1

first reported by Stratton and Busch.[3–5] These authors also discussed the subsequent formation of a mononuclear complex of the formula ML_2X_2. In studies of the iron(II) and nickel(II)

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complexes of bis(2-pyridylmethyl) ketazine, pmk (**1**, R = CH$_3$), Stratton pointed out that complexes of the binuclear or mononuclear composition are consistent with the coordination capabilities of *trans,trans*-pmk (**2**) or *cis,trans*-pmk (**3**), respectively.[6,7] Complexes of the third possible stereoisomer, *cis,cis*-pmk (**4**), have not yet been observed because they are

cis,trans-pmk
3

cis,cis-pmk
4

trans,trans-pmk
2
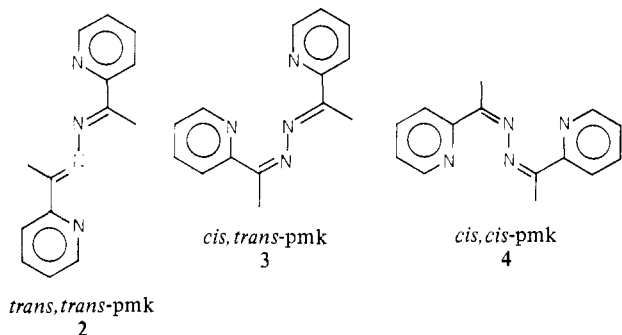
believed to be sterically unstable relative to the complexes of the other stereoisomers. More recent papers on the magnetic resonance spectra of binuclear complexes of bis(2-pyridyl-methyl) ketazine also report the observation of a mixed-metal analogue (i.e., M(pmk)$_3$M'X$_4$).[11]

To date, there has been no structural investigation of the complexes of bis(2-pyridylmethyl) ketazine. The only magnetic study of these complexes is a variable-temperature (80–300 K) susceptibility investigation of the binuclear nickel(II) complexes of bis(2-pyridyl) ketazine, pk (**1**, R = H).[10] Magnetic data for Ni$_2$(pk)(NO$_3$)$_4$ indicated the existence of antiferromagnetic coupling between the nickel(II) centers, but the interaction was not strong enough to exhibit a maximum in the susceptibility above 80 K.

The complexes of bis(pyridylmethyl) ketazine are attractive systems for structural and magnetic studies because the close proximity of the metal(II) ions implies a strong likelihood of magnetic coupling. In addition, these complexes exhibit a bridging route that consists of a polyatomic direct bonding pathway and a conjugated bonding structure throughout the ligand. The investigations of binuclear complexes connected by a pathway involving two or more atoms in a conjugated bonding configuration have become more numerous in recent years.[13-25] The nature of magnetic and electronic interactions in magnetically coupled systems is the object of much speculation,[21-24] but with the rapid growth in the number of reference complexes, more information is being obtained. The structural and magnetic study of the complexes of bis(pyridyl) ketazine promises to be a useful addition to the study of

magnetic coupling propagated via a polyatomic conjugated pathway.

The complexes that we investigate in this report result from the coordination of bis(2-pyridylmethyl) ketazine to copper(II) chloride and copper(II) nitrate. The latter complex consists of isolated monomers of the general formula Cu(pmk)(NO$_3$)$_2$, and the material exhibits no significant magnetic coupling over the studied temperature range (6–300 K). The former complex is binuclear with the formula Cu$_2$(pmk)Cl$_4$ and exhibits antiferromagnetic exchange with an excited triplet energy level some 52 cm^{-1} above a ground-state singlet.

An interesting result of our structural study is also the confirmation of different stereoisomeric forms of the ligand coordinated to copper(II) in the two complexes. Our results confirm the earlier predictions of Stratton et al. based on synthetic and spectral studies of the analogous complexes of copper(II) and pk (**1**, R = H).[6] We report here the synthesis, room-temperature crystal structure, and variable-temperature (6–300 K) powder magnetic susceptibility for Cu(*cis,trans*-pmk)(NO$_3$)$_2$ and Cu$_2$(*trans,trans*-pmk)Cl$_4$.

Experimental Section

Syntheses. Bis(2-pyridylmethyl) Ketazine, pmk. The method of Stratton[7] was followed in the preparation of pmk. The product was recrystallized by dissolving in hot ethanol, adding water, and cooling, yielding yellow needle crystals. No attempt was made to separate stereoisomers of pmk at this time.

Cu(*cis,trans*-pmk)(NO$_3$)$_2$. A stoichiometric amount of pmk in methanol was added to a refluxing solution of copper(II) nitrate in methanol, and the solution was refluxed for several hours. The solution was filtered (removing a small amount of green precipitate) and allowed to stand in a covered beaker. Well-developed, nearly black, dark green crystals of Cu(*cis,trans*-pmk)(NO$_3$)$_2$ were obtained after several days. Anal. calcd for CuC$_{14}$H$_{14}$N$_6$O$_6$: Cu, 14.92; C, 39.49; H, 3.31; N, 19.73; O, 22.54. Found: Cu, 14.63; C, 38.86; H, 3.51; N, 19.24.

Cu$_2$(*trans,trans*-pmk)Cl$_4$. Stoichiometic quantities of pmk and copper(II) chloride were allowed to react in hot ethanol. The product crystallized immediately as a fine powder. The powder was used for susceptibility measurements. Anal. Calcd for CuC$_7$H$_7$N$_2$Cl$_2$: Cu, 25.06; C, 33.15; H, 2.78; N, 11.05; Cl, 27.96. Found: Cu, 25.02; C, 33.12; H, 3.00; N, 11.11.

Single crystals suitable for crystal structure determination were obtained by connecting an ethanol solution of pmk to an ethanolic solution of copper(II) chloride via a solvent bridge. Well-developed single crystals were formed by the diffusion of the solutes through the solvent bridge.

Magnetic Data. Magnetic susceptibility data were recorded over the temperature range 6–300 K with an alternating force magnetometer (AFM). Operation and calibration procedures are summarized elsewhere.[25] The temperature-dependent magnetic data are listed in Table I (supplementary material).

Crystal Structure Determinations

Data Collection for Cu(pmk)(NO$_3$)$_2$. Data were obtained from a dark green crystal of dimensions 0.46 × 0.52 × 0.60 mm on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Cell dimensions were determined from the angular settings of 25 accurately centered reflections having 15° $\leq \theta \leq$ 16°. Crystal data: CuC$_{14}$H$_{14}$N$_6$O$_6$, M_r = 425.8, monoclinic space group C2/c, a = 11.356 (4) Å, b = 17.325 (5) Å, c = 8.829 (2) Å, β = 91.61 (3)°, Z = 4, d_{calcd} = 1.629 g cm^{-3}, μ(Mo Kα) = 13.6 cm^{-1}. Intensity data were collected by the θ–2θ-scan method employing variable scan rates designed to yield $I \simeq 25\sigma(I)$ for all significant data. Scan rates, determined in a 10° min^{-1} prescan, ranged from 0.833 to 10.0° min^{-1}. All data in one quadrant having $h + k$ even and 1° $\leq \theta \leq$ 25° were measured in this fashion. No decline in the intensities of 3 periodically remeasured reflections nor movement of two periodically recentered reflections was noted. Of 1534 unique data measured, 988 had $F^2 > 3\sigma(F^2)$ and were used in the refinement. Background, Lorentz, and polarization corrections were applied. Variation in the intensities of reflections near χ = 90° during ψ scans was less than 4%, and thus no absorption correction was applied.

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Table II

(a) Coordinates and Refined Thermal Parameters for Non-Hydrogen Atoms of Cu(pmk)(NO$_3$)$_2$

atom	x	y	z	B_{iso}, A^2	atom	x	y	z	B_{iso}, A^2
Cu	$^1/_2$	0.16863 (6)	$^3/_4$		C(2)	0.3676 (7)	0.2528 (5)	1.1572 (9)	
O(1)	0.3890 (5)	0.0737 (3)	0.6794 (7)		C(3)	0.3351 (8)	0.1864 (5)	1.2324 (9)	
O(2)	0.2830 (7)	0.1668 (3)	0.6003 (8)		C(4)	0.3523 (8)	0.1178 (5)	1.1675 (9)	
O(3)	0.2359 (7)	0.0524 (5)	0.5479 (12)		C(5)	0.4001 (8)	0.1129 (5)	1.0268 (9)	
N(1)	0.4325 (6)	0.1768 (3)	0.9518 (7)		C(6)	0.4511	0.3276	0.9441	7.0
N(2)	0.4887	0.3394	0.8205	6.3	C(7)	0.4403	0.3962	1.0428	9.2
N(3)	0.5087	0.2850	0.7327	7.2	C(8)	0.4468	0.3121	0.9274	7.0
N(4)	0.3000 (6)	0.0977 (4)	0.6108 (8)		C(9)	0.5556	0.3949	0.5115	7.4
C(1)	0.4168 (7)	0.2453 (4)	1.0162 (8)						

(b) Coordinates for Hydrogen Atoms of Cu(pmk)(NO$_3$)$_2$

atom	x	y	z	atom	x	y	z
H(2)	0.3575	0.3035	1.2037	H(4)	0.3309	0.0697	1.2220
H(3)	0.2978	0.1902	1.3335	H(5)	0.4101	0.0634	0.9814

(c) Coordinates for Non-Hydrogen Atoms of Cu$_2$(pmk)Cl$_4$

atom	x	y	z	atom	x	y	z
Cu(1)	0.5134 (1)	0.24554 (7)	0.37548 (7)	C(3)	0.1747 (9)	0.4018 (6)	0.5225 (5)
Cu(2)	0.3227 (1)	0.25812 (7)	0.09573 (7)	C(4)	0.2723 (9)	0.3322 (6)	0.5721 (5)
Cl(1)	0.5838 (2)	0.1250 (1)	0.4783 (1)	C(5)	0.3666 (8)	0.2847 (5)	0.5298 (5)
Cl(2)	0.6276 (2)	0.1823 (2)	0.2729 (1)	C(6)	0.2927 (8)	0.3926 (5)	0.3016 (4)
Cl(3)	0.2535 (2)	0.1456 (1)	-0.0151 (1)	C(7)	0.1810 (9)	0.4525 (6)	0.2319 (5)
Cl(4)	0.1944 (2)	0.1929 (2)	0.1897 (1)	C(8)	0.5415 (8)	0.4012 (5)	0.1819 (4)
N(1)	0.3723 (6)	0.3050 (4)	0.4421 (4)	C(9)	0.6462 (10)	0.4603 (6)	0.2558 (5)
N(2)	0.4104 (6)	0.3518 (4)	0.2850 (4)	C(10)	0.5629 (8)	0.3899 (5)	0.0894 (4)
N(3)	0.4277 (7)	0.3557 (4)	0.1945 (4)	C(11)	0.6718 (8)	0.4378 (5)	0.0580 (5)
N(4)	0.4665 (6)	0.3259 (4)	0.0349 (4)	C(12)	0.6810 (9)	0.4209 (6)	-0.0312 (5)
C(1)	0.2774 (8)	0.3741 (5)	0.3954 (5)	C(13)	0.5838 (9)	0.3576 (6)	-0.0876 (5)
C(2)	0.1784 (9)	0.4218 (6)	0.4333 (5)	C(14)	0.4760 (9)	0.3110 (6)	-0.0524 (5)

(d) Coordinates and Refined Thermal Parameters for Hydrogen Atoms of Cu$_2$(pmk)Cl$_4$

atom	x	y	z	B_{iso}, A^2	atom	x	y	z	B_{iso}, A^2
H(2)	0.1117	0.4733	0.3966	6.0 (2)	H(91)	0.6660	0.5195	0.2285	5.0 (2)
H(3)	0.1067	0.4351	0.5498	8.0 (3)	H(92)	0.7421	0.4330	0.2824	11.0 (3)
H(4)	0.2687	0.3163	0.6330	7.0 (2)	H(93)	0.6006	0.4796	0.3038	4.0 (2)
H(5)	0.4329	0.2363	0.5658	5.0 (2)	H(11)	0.7399	0.4816	0.0976	3.0 (2)
H(71)	0.0820	0.4375	0.2285	12.0 (4)	H(12)	0.7585	0.4537	-0.0536	5.0 (2)
H(72)	0.1926	0.4488	0.1718	6.0 (2)	H(13)	0.5918	0.3459	-0.1490	7.0 (2)
H(73)	0.1907	0.5188	0.2518	11.0 (3)	H(14)	0.4991	0.2652	-0.0923	4.0 (2)

Structure Solution and Refinement of Cu(pmk)(NO$_3$)$_2$. Systematic absences hkl with $h + k$ odd and $h0l$ with l odd limit the space group to either Cc or $C2/c$. The Patterson map was interpreted in terms of a Cu position on the twofold axis at $^1/_2$, y, $^3/_4$ in $C2/c$. Difference Fourier syntheses revealed the positions of an ordered nitrato ligand and an ordered pyridyl ring in general positions; however the central portion of the pmk ligand is disordered about the twofold axis, yielding half-populated positions for the six atoms C(6)–C(9), N(2), and N(3). Efforts to break the symmetry into an ordered structure in Cc did not result in any model that could be successfully refined by least-squares methods to yield significantly better agreement with the data. Since the geometry and thermal parameters of the ordered region in $C2/c$ are quite reasonable, we took this to be the apparent space group.

In the refinement, the ordered atoms were treated anisotropically, but disordered atoms could not be refined by least-squares methods due to near-coincidences in coordinates of partially populated positions. The positions and isotropic thermal parameters of these atoms were adjusted from residuals in difference maps. pyridyl hydrogen atoms were placed in calculated positions as fixed contributions with B = 7 A^2. Full-matrix least-squares refinement was based upon F with unit weights and coverged with R = 0.079. The largest residual in a final difference map was 0.55 e A^{-3}, located in the disordered region near the overlapping C–C(methyl) bonds.

Data Collection for Cu$_2$(pmk)Cl$_4$. Data collection from a crystal of dimensions 0.06 × 0.14 × 0.20 mm was carried out in a fashion similar to that employed for Cu(pmk)(NO$_3$)$_2$. Cu Kα radiation (λ = 1.541 84 Å) was employed. Crystal data: Cu$_2$Cl$_4$C$_{14}$H$_{14}$N$_4$, M_r = 507.2, monoclinic space group $P2_1/n$, a = 9.058 (2) Å, b = 14.115 (3) Å, c = 14.892(3) Å, β = 106.26 (2), Z = 4, d_{calcd} = 1.843 g cm^{-3}, μ(Cu Kα) = 83.15 cm^{-1}. Specifics of this data collection: precision

$I \simeq 50\sigma(I)$, scan rates 0.33–10.0° min^{-1}, one quadrant of data collected with $2° \leq \theta \leq 70°$. Empirical absorption corrections were applied, on the basis of ψ scans of reflections near χ = 90°. The minimum relative transmission coefficient was 67.9%; the average value was 87.7%. Of 3449 unique data thus measured, 1911 had $F^2 > 3\sigma(F^2)$ and were used in the refinement.

Structure Solution and Refinement Cu$_2$(pmk)Cl$_4$. The structure was solved by heavy-atom methods and refined by full-matrix weighted least squares. Statistical weights were employed, including the factor p = 0.05. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located by difference maps and included in fixed positions with refined isotropic thermal parameters. Convergence was achieved with R = 0.055, R_w = 0.079, and "goodness of fit" = 2.64. The maximum residual in a final difference map was 0.53 e Å^{-3}, near a Cu position.

Results and Discussion

Final positional parameters for Cu(*cis,trans*-pmk)(NO$_3$)$_2$ and Cu$_2$(*trans,trans*-pmk)Cl$_4$ are given in Table II. Thermal parameters are given in Table III (supplementary material). Tables IV and V contain the bond lengths and angles. The digits in parentheses are the estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix in the course of least-squares refinement.

The Cu(*cis,trans*-pmk)(NO$_3$)$_2$ complex is monomeric with pmk acting as a planar tridentate ligand and the N(2) position is uncoordinated. The molecule lies on a crystallographic $C2$ axis (space group $C2/c$), which leads to half-populated positions for the six atoms; however, the Cu atom, nitrate ions, and aromatic rings are ordered. This disorder has limited the

Table IV. Bond Distances (Å)

Cu(pmk)(NO₃)₂ᵃ

Cu-N(1)	1.964 (4)	C(4)-C(5)	1.372 (6)
Cu-N(3)	2.03	C(6)-C(7)	1.48
Cu-O(1)	2.154 (3)	C(6)-N(2)	1.20
Cu-O(2)	2.764 (5)	N(2)-N(3)	1.25
N(1)-C(1)	1.330 (5)	N(3)-C(8)	1.58
N(1)-C(5)	1.347 (6)	C(8)-C(9)	1.53
C(1)-C(2)	1.385 (6)	C(8)-C(1)	1.44
C(1)-C(6)	1.61	O(1)-N(4)	1.235 (5)
C(2)-C(3)	1.384 (7)	O(2)-N(4)	1.217 (5)
C(3)-C(4)	1.335 (7)	O(3)-N(4)	1.197 (6)

Cu₂(pmk)Cl₄

Cu(1)-Cl(1)	2.259 (1)	N(4)-C(14)	1.344 (6)
Cu(1)-Cl(2)	2.254 (1)	C(1)-C(2)	1.364 (7)
Cu(1)-N(1)	2.008 (4)	C(1)-C(6)	1.466 (6)
Cu(1)-N(2)	2.057 (4)	C(2)-C(3)	1.367 (7)
Cu(2)-Cl(3)	2.250 (1)	C(3)-C(4)	1.388 (8)
Cu(2)-Cl(4)	2.252 (1)	C(4)-C(5)	1.370 (7)
Cu(2)-N(3)	2.046 (4)	C(6)-C(7)	1.493 (7)
Cu(2)-N(4)	2.023 (4)	C(8)-C(9)	1.490 (6)
N(1)-C(1)	1.355 (6)	C(8)-C(10)	1.452 (6)
N(1)-C(5)	1.352 (6)	C(10)-C(11)	1.381 (6)
N(2)-C(6)	1.294 (6)	C(11)-C(12)	1.375 (7)
N(2)-N(3)	1.401 (5)	C(12)-C(13)	1.365 (8)
N(3)-C(8)	1.272 (6)	C(13)-C(14)	1.396 (7)
N(4)-C(10)	1.356 (5)		

ᵃ Distances involving disordered atoms (given without esd's) are based on assigned coordinates and are approximate.

Table V. Bond Angles (deg)

Cu(pmk)(NO₃)₂

N(1)-Cu-N(1')	171.8 (2)	N(1)-C(1)-C(2)	122.1 (4)
N(1)-Cu-O(1)	94.4 (2)	N(1)-C(1)-C(6)	126
N(1)-Cu-O(1')	91.9 (2)	C(6)-C(1)-C(2)	112
N(1)-Cu-N(3)	91	C(1)-C(2)-C(3)	118.2 (4)
O(1)-Cu-O(1')	80.4 (2)	C(2)-C(3)-C(4)	119.4 (4)
O(1)-Cu-N(3)	140	C(3)-C(4)-C(5)	120.7 (5)
O(1')-Cu-N(3)	139	C(4)-C(5)-N(1)	121.0 (5)
N(1')-Cu-N(3)	81	C(1)-C(6)-C(7)	117
Cu-O(1)-N(4)	110.4 (3)	C(1)-C(6)-N(2)	127
O(1)-N(4)-O(2)	119.7 (5)	C(7)-C(6)-N(2)	116
O(1)-N(4)-O(3)	119.1 (5)	C(6)-N(2)-N(3)	121
O(2)-N(4)-O(3)	121.1 (6)	N(2)-N(3)-C(8)	114
Cu-N(1)-C(1)	120.8 (3)	N(3)-C(8)-C(9)	127
Cu-N(1)-C(5)	120.4 (3)	N(3)-C(8)-C(1')	109
Cu-N(3)-C(8)	99	C(7)-C(8)-C(1')	109
Cu-N(3)-N(2)	134	C(8)-C(1')-N(1')	117
C(1)-N(1)-C(5)	118.8 (4)	C(8)-C(1')-C(2')	121

Cu₂(pmk)Cl₄

Cl(1)-Cu(1)-Cl(2)	93.72 (5)	Cu(2)-N(4)-C(14)	125.7 (4)
Cl(1)-Cu(1)-N(1)	94.5 (1)	C(10)-N(4)-C(14)	118.6 (4)
Cl(1)-Cu(1)-N(2)	169.6 (1)	N(1)-C(1)-C(2)	122.6 (4)
Cl(2)-Cu(1)-N(1)	167.5 (1)	N(1)-C(1)-C(6)	113.7 (4)
Cl(2)-Cu(1)-N(2)	93.2 (1)	C(2)-C(1)-C(6)	123.8 (4)
N(1)-Cu(1)-N(2)	77.5 (2)	C(1)-C(2)-C(3)	119.9 (5)
Cl(3)-Cu(2)-Cl(4)	94.65 (6)	C(2)-C(3)-C(4)	118.5 (5)
Cl(3)-Cu(2)-N(3)	168.9 (1)	C(3)-C(4)-C(5)	119.2 (5)
Cl(3)-Cu(2)-N(4)	95.0 (1)	C(4)-C(5)-N(1)	122.5 (5)
Cl(4)-Cu(2)-N(3)	92.6 (1)	C(1)-C(6)-N(2)	113.9 (4)
Cl(4)-Cu(2)-N(4)	168.8 (1)	C(1)-C(6)-C(7)	122.5 (5)
N(3)-Cu(2)-N(4)	77.0 (2)	N(2)-C(6)-C(7)	123.6 (5)
Cu(1)-N(1)-C(1)	116.6 (4)	N(3)-C(8)-C(9)	123.2 (5)
Cu(1)-N(1)-C(5)	126.1 (4)	N(3)-C(8)-C(10)	114.4 (4)
C(1)-N(1)-C(5)	117.3 (4)	C(9)-C(8)-C(10)	122.4 (4)
Cu(1)-N(2)-C(6)	116.5 (4)	N(4)-C(10)-C(8)	114.0 (4)
Cu(1)-N(2)-N(3)	120.4 (4)	C(8)-C(10)-C(11)	124.4 (4)
C(6)-N(2)-N(3)	119.1 (4)	N(4)-C(10)-C(11)	121.6 (4)
Cu(2)-N(3)-N(2)	120.7 (3)	C(10)-C(11)-C(12)	119.0 (5)
Cu(2)-N(3)-C(8)	117.8 (4)	C(11)-C(12)-C(13)	120.3 (5)
N(2)-N(3)-C(8)	118.4 (4)	C(12)-C(13)-C(14)	118.4 (5)
Cu(2)-N(4)-C(10)	115.7 (4)	C(13)-C(14)-N(4)	122.1 (5)

precision of the structure determination somewhat, since the positions of the atoms in the disordered region could not be refined by the usual least-squares procedures. The nitrate
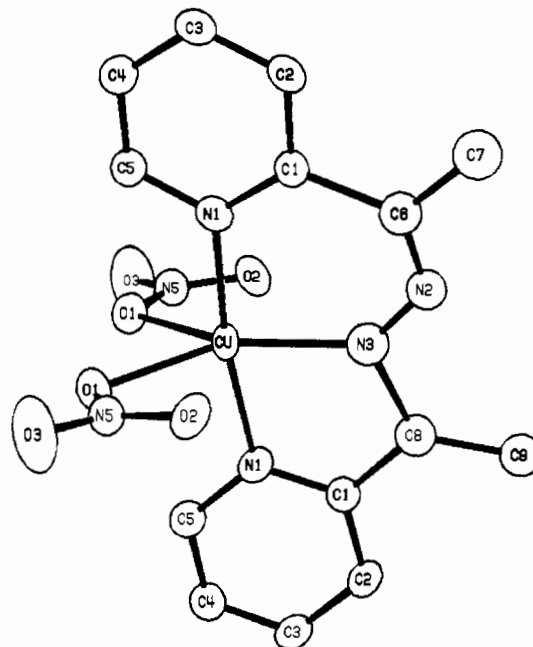

Figure 1. Molecular structure of Cu(*cis,trans*-pmk)(NO₃)₂, illustrating the atom-numbering scheme. The hydrogen atoms are omitted.

Table VI. Distances and Angles for the Elongated Cu-Cl Contacts in Cu₂(*trans,trans*-pmk)Cl₄

atoms	dist, Å	atoms	angle, deg
Cu(1)-Cl(3)ᵃ	2.785 (1)	Cu(1)-Cl(1)-Cu(2)ᵃ	90.08 (4)
Cu(1)-Cl(4)ᵇ	3.475 (1)	Cu(1)-Cl(2)-Cu(2)ᵇ	88.54 (4)
Cu(2)-Cl(1)ᵃ	2.889 (1)	Cu(1)-Cl(3)-Cu(2)ᵃ	92.96 (4)
Cu(2)-Cl(2)ᵇ	3.414 (1)	Cu(1)-Cl(4)-Cu(2)ᵇ	87.04 (4)

ᵃ Intermolecular. ᵇ Intramolecular.

ligands are pseudobidentate with Cu-O distances of 2.15 and 2.76 Å. Considering only the closest nitrate oxygen, the geometry of the copper(II) ion may be described as a highly distorted trigonal bipyramid with O(1) and N(3) lying in the trigonal plane. There are no intermolecular contacts less than 3.33 Å and no intermolecular Cu⋯Cu distance less than 7.32 Å. Figure 1 shows an ORTEP diagram of the molecular unit, and Figure 2 shows the molecular packing in the unit cell.

The binuclear complex Cu₂(*trans,trans*-pmk)Cl₄ has each of the coordinating positions of the pmk ligand attached to a copper(II) ion. The bridge connecting the two metal centers consists of an azine linkage. Though the ligand is conjugated, it is not planar. There is a rotation about the N-N bond, which results in a Cu-N-N-Cu torsion angle of 70.8°.

Figure 3 shows an ORTEP diagram of the binuclear molecule. The four metal-ligand bonds about the copper(II) ion result in a planar coordination geometry. However, each copper(II) also has an elongated intramolecular contact and an elongated intermolecular contact, both to chlorine atoms, forming a tetragonally distorted octahedral coordination sphere. The elongated Cu-Cl contact distances and Cu-Cl-Cu bridging angles are listed in Table VI. The internuclear separation of the two copper(II) ions is 4.04 Å *intra*molecular and 3.67 Å *inter*molecular. Figure 4 shows a stereoscopic packing diagram of the unit cell.

No attempt was made to isolate the various stereoisomers of bis(2-pyridylmethyl) ketazine before reacting the ligand with the copper(II) salts. Previously, other workers have unsuccessfully attempted to separate the stereoisomers and have come to the conclusion that the stable form of the free pmk ligand is the trans,trans isomer.[5-8] The cis,trans isomer is generated by a template rearrangement reaction of the solvated ligand by solvated metal ions. The cis,trans isomer is stable
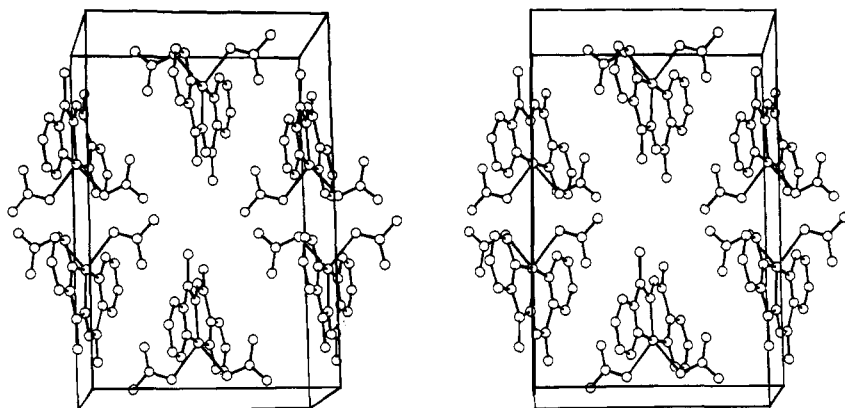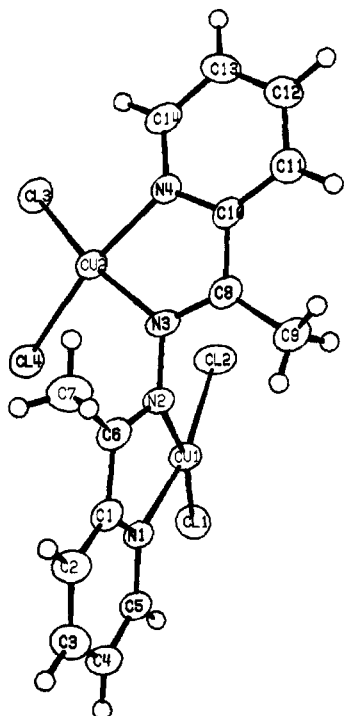
Figure 2. Stereoview packing diagram for Cu(*cis,trans*-pmk)(NO₃)₂.

Figure 3. Structure of Cu₂(*trans,trans*-pmk)Cl₄, illustrating the atom-numbering scheme.

when coordinated to a metal ion. The rearrangement of the ligand that occurs in the synthesis of Cu(*cis,trans*-pmk)(NO₃)₂ cannot take place in the synthesis of the chloride analogue since Cu₂(*trans,trans*-pmk)Cl₄ precipitates upon formation; there is insufficient time for rearrangement of the ligand in the chloride complex. The nitrate complex on the other hand is soluble, and the support of this molecule by the solution

permits the rearrangement to take place.

The magnetic susceptibility data for Cu(*cis,trans*-pmk)-(NO₃)₂ are shown in Figure 5 as inverse magnetic susceptibility and effective magnetic moment [$\mu_{eff} = (7.997\chi T)^{1/2}$] plotted as a function of temperature. The nearly linear form of the plots in Figure 5 is consistent with the simple Curie–Weiss law, shown in eq 1, where all of the parameters have their usual

$$\chi = \frac{Ng^2\mu_B^2}{3K} \frac{S(S+1)}{T-\Theta} \tag{1}$$

meaning. The line through the points in Figure 5 is the best fit of the data to eq 1 with the parameters $g = 2.22 \pm 0.02$ and $\Theta = -1.2 \pm 0.2$ K. The small value for Θ is expected since the structure consists of essentially noninteracting monomers, which result in the absence of significant magnetic exchange.

The magnetic susceptibility and effective magnetic moment of Cu₂(*trans,trans*-pmk)Cl₄ are plotted in Figure 6 as a function of temperature. The magnetic susceptibility exhibits a broad maximum around 50 K and rapidly drops toward zero as the temperature is lowered. This type of temperature-dependent behavior is expected for an antiferromagnetically coupled copper(II) binuclear molecule. The spin Hamiltonian, which describes the coupling of two neighboring spins, is shown in eq 2.

$$\mathcal{H} = -2J S_1 \cdot S_2 \tag{2}$$

The magnetic susceptibility may be calculated for a spin $S_1 = S_2 = {}^1/_2$ binuclear complex using the equation

$$\chi = \frac{2Ng^2\mu_B^2}{kT} \frac{e^{-x}}{1 + 3e^{-x}} \tag{3}$$

where $x = 2J/kT$, and $2J$ is the energy of the splitting between the magnetically coupled triplet and singlet states. The small increase in the magnetic susceptibility as the temperature is lowered at the lowest temperatures is consistent with a small
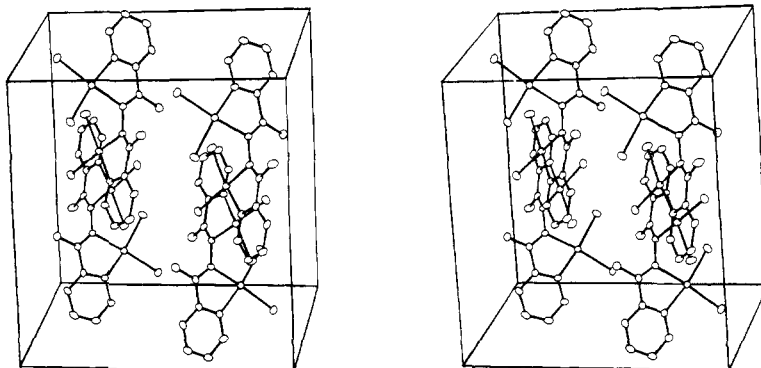

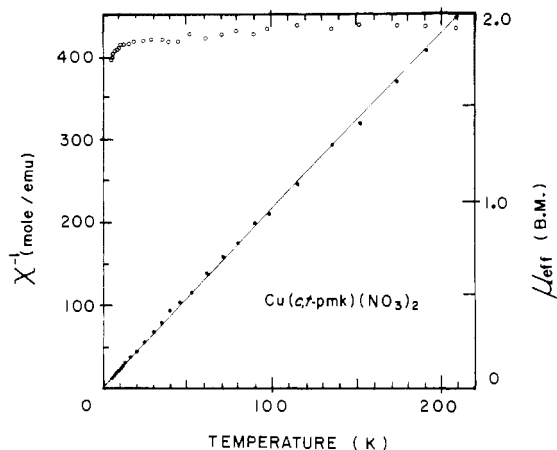**Figure 4.** Stereoview packing diagram for Cu₂(*trans,trans*-pmk)Cl₄.

Figure 5. Inverse magnetic susceptibility and effective magnetic moment plotted as a function of temperature for Cu(*cis,trans*-pmk)(NO$_3$)$_2$. The line through the points is the best fit of the data to the Curie–Weiss law as described in text.
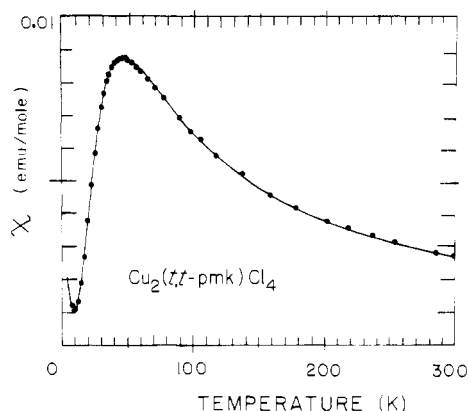

Figure 6. Magnetic susceptibility plotted as a function of temperature for Cu$_2$(*trans,trans*-pmk)Cl$_4$. The curve through the data is the best fit of the data to eq 2 as described in text.

paramagnetic (mononuclear) impurity. In fitting the data to theoretical models, a correction term was added corresponding to a 1% mononuclear copper(II) concentration. The curves through the data points in Figure 6 are obtained from the best fit of the data to eq 3 with the parameters $g = 2.10 \pm 0.02$ and $J = -26 \pm 2$ cm^{-1}.

Magnetic coupling in the binuclear complex Cu$_2$(*trans,-trans*-pmk)Cl$_4$ may be propagated through the Cu–N–N–Cu azine exchange pathway or either of the Cu–Cl–Cu exchange pathways. Since the structure data show the pmk ligand to be nonplanar, a mechanism of propagation through the azine linkage is very likely a σ-bonded overlap pathway without the benefit of π overlap. The proposed structures of the previously reported pmk binuclear complexes of the formula M$_2$-(*trans,trans*-pmk)$_3$X$_4$ are required by structural constraints to also have a nonplanar geometry for the bridging pmk ligand. There is no such structural constraint in the binuclear complex Cu$_2$(*trans,trans*-pmk)Cl$_4$; nevertheless a nonplanar geometry exists. The nonplanar geometry is necessary to accommodate the copper–chlorine contacts.

It is interesting to speculate that the elongated contacts might help to promote the antiferromagnetic coupling. Hatfield and co-workers[26] have proposed an empirical relationship between the coupling constant J and some structural parameters of chlorine-bridged copper(II) dimers. The structural parameters are expressed as the ratio of the interplanar distance (r) to the Cu–Cl–Cu bridging angle (ϕ). From a curve of ϕ/r plotted vs. J, the exchange values that are predicted from the bridging chlorine contacts are an antiferromagnetic intradimer contribution to J and a ferromagnetic interdimer exchange J'. It is important to note that the fitted curve shown in Figure 6 did not require a correction for interdimer magnetic coupling. The intermolecular chlorine-bridging contact is the shorter of the two types of Cu–Cl–Cu contacts; however, there is no apparent need for a ferromagnetic interdimer correction to the data. We believe it is unlikely that either of the elongated Cu–Cl contacts are contributing substantially to the overall magnetic exchange and that propagation of magnetic coupling is via the direct ketazine pathway resulting in intramolecular antiferromagnetic exchange.

(26) Hatfield, W. E.; Weller, R. R.; Hall, J. W. *Inorg. Chem.* **1980**, *19*, 3825.