bond to, tetraamine complexes with simple amine ligands will be unstable and will not form. In the case of amines with long alkyl groups which are better bases than ethylamine, steric factors account for the instability.

Acknowledgment. This work was supported by a Cottrel Grant from the Research Corp. Support from the University of Kentucky for computer costs is also gratefully acknowledged.

Registry No. $[Pt(NH_3)_4Cl](HSO_4)_2$, 76687-77-9; $[Pt(NH_3)_4]Cl_2$, 13933-32-9.

Supplementary Material Available: Listings of structure factor amplitudes (Table IV) and thermal parameters (Table V) (6 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, La Trobe University, Victoria, Australia, and Monash University, Victoria, Australia, and the Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, Australia

Magnetic Interactions in Metal Complexes of Pentadentate Binucleating Ligands. 1. Synthesis and Properties of Binuclear Copper(II) Compounds Containing Single-Atom Bridging Ligands. Crystal and Molecular Structure of a Binuclear μ-Hydroxo-Bridged Copper(II) Complex of 1,5-Bis[1-(pyridin-2-yl)ethylideneamino]pentan-3-ol

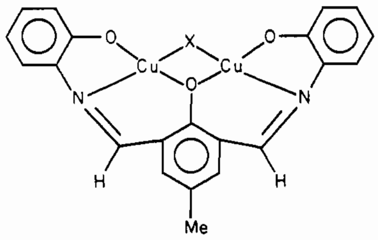
WALDEMAR MAZUREK,[1a] KEVIN J. BERRY,[1b] KEITH S. MURRAY,[1b] MAXWELL J. O'CONNOR,*[1a]
MICHAEL R. SNOW,[1c] and ANTHONY G. WEDD[1a]

Received August 25, 1981

A series of binuclear copper(II) complexes based on some new binucleating ligands derived from condensation of salicylaldehyde, pyridine-2-carboxaldehyde, and pyrrole-2-carboxaldehyde with 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol are reported. The compounds feature a bridging ligand alkoxide group and an additional single-atom bridging ligand X (X = OH, OR, Cl, Br). The crystal and molecular structure of the μ-hydroxo-bridged dicopper(II) complex of 1,5-bis[1-pyridin-2-yl)ethylideneamino]pentan-3-ol isolated as the perchlorate salt of formula $C_{17}H_{22}N_4O_{11}Cl_2Cu_2$ having space group *Pbca* and unit cell dimensions $a = 12.287$ (14) Å, $b = 12.000$ (6) Å, and $c = 15.487$ (8) Å was solved with 2202 nonzero structure factors with $I \geq 2.50(I)$. Refinement by blocked-matrix least-squares methods gave a final R factor of 0.0405. The binucleating nature of the ligand was thus established, the two copper(II) ions being bridged by the secondary alkoxo group of the ligand and an additional hydroxo group. The N_2O_2-donor atom sets around each copper are essentially planar. Both copper atoms may be regarded as having square-pyramidal coordination, one being coordinated to a water molecule and the other having an interaction (Cu–O = 2.234 Å) with the oxygen atom of the bridging OH group of a neighboring binuclear unit. The structure thus involves *pairs of binuclear units*. The intramolecular Cu···Cu separation is 2.928 Å. Magnetic susceptibilities of the solid complexes were determined over the temperature range 4.2–300 K. Generally the magnetic behavior conforms closely to the Bleaney–Bowers equation for a spin-coupled $S = {}^1/_2$ system in which the singlet–triplet separation is $2J$. In some cases a tetramer model was found to give slightly improved fits and yield physically more reasonable g values than were obtained with the Bleaney–Bowers equation. The title compound shows significant intramolecular antiferromagnetic coupling with a best fit J value, $-142\ \text{cm}^{-1}$, deduced from both theoretical models. The coupling in the other compounds is shown to be dependent on the nature of the bridging group, the chain length of the ligand backbone, and the extent of saturation of the C–N linkages of the ligands, all of which probably lead to significant structural changes around the copper(II) ions and hence influence the magnetic coupling of the two copper centers. The first examples of ferromagnetic coupling in copper(II) complexes of binucleating ligands of this type are reported.

Introduction

Robson[2] initially designed and synthesised pentadentate binucleating ligands derived from the reaction of 2-aminophenol and 2,6-diformyl-4-methylphenol and isolated complexes of various metals including Cu(II). The formulation **1** featuring a bridging phenoxo group and the additional bridging ligand X is now firmly established. The original ligand has been modified extensively,[2-4] and the ligand X may donate one (OR^-, Cl^-, etc.) or two (e.g., pyrazolate) atoms to the coordination spheres of the metals.



1

A number of these binuclear copper(II) species have magnetic properties which indicate considerable antiferromagnetic spin exchange between the copper ($S = {}^1/_2$) centers. Variation of the magnitude of this exchange with bridging group X and with the nature of the backbone of the pentadentate ligand has been investigated.[2-4] The occurrence of both antiferromagnetic and ferromagnetic exchange has been noted in a large number of binuclear copper(II) systems,[5-7] but no examples of ferromagnetic coupling have been reported for compounds of the type **1**. Recent studies[8,9] report binuclear

---

(1) (a) La Trobe University. (b) Monash University. (c) University of Adelaide.

(2) (a) Robson, R. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 125–128. (b) Robson, R. *Aust. J. Chem.* **1970**, *23*, 2217–2224. (c) Hoskins, B. F.; Robson, R.; Schaap, H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 21–25. (d) McFadden, W. D.; Robson, R.; Schaap, H. *Inorg. Chem.* **1972**, *11*, 1777–1785. (e) Dickson, I. E.; Robson, R. *Ibid.* **1974**, *13*, 1301–1306.

(3) (a) Okawa, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3019. (b) Okawa, H.; Kida, S. *Ibid.* **1971**, *44*, 1172. (c) Okawa, H.; Kida, S.; Muto, Y.; Tokii, T. *Ibid.* **1972**, *45*, 2480–2484. (d) Okawa, H.; Toku, T.; Nonaka, Y.; Muto, Y.; Kida, S. *Ibid.* **1973**, *46*, 1462–1465.

(4) Casellato, U.; Vigato, P. A.; Vidali, M. *Coord. Chem. Rev.* **1977**, *23*, 31–117.

(5) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173–241.

(6) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209–231.

(7) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313–347.

0020-1669/82/1321-3071$01.25/0 © 1982 American Chemical Society

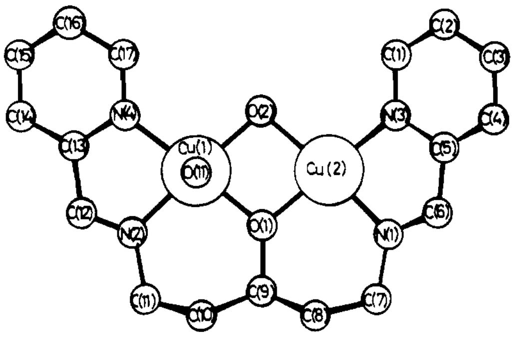
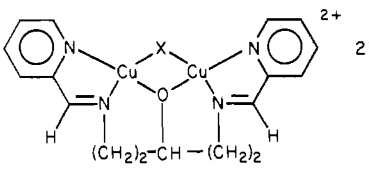


Figure 1. Atom numbering scheme for the cation in compound **2a**.

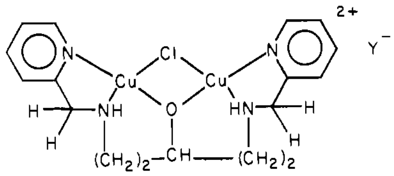
copper(II) complexes of pentadentate ligands derived from 2,6-diformyl-4-methylphenol and containing heterocyclic amine nitrogen donor atoms and various bridging groups. Strong antiferromagnetic coupling of the $S = {}^1/_2$ copper(II) was observed.

Current interest in binuclear copper centers derives from their apparent presence in the dioxygen-binding protein hemocyanin[10-13] and the various multicopper oxidases.[14] Recent EXAFS studies[12c] have shown that each copper ion in oxyhemocyanin is coordinated to two imidazolato nitrogen atoms although the nature of the endogenous bridging group responsible for the exchange interaction between the two copper atoms, and hence the considerable antiferromagnetic coupling ($2J = -550$ cm^{-1}) in oxyhemocyanin, has not been revealed. The phenoxide group of tyrosine has been favored for this role, but there appears to be no convincing evidence for this claim.[12b,c] In fact, the complexes reported in the present and related studies[15] indicate that an alkoxo group could also be considered as a candidate.

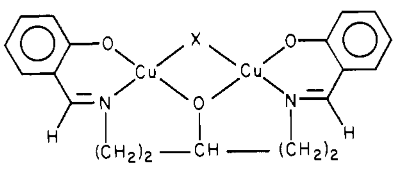
The pentadentate binucleating ligands reported here are stereochemically more flexible than the corresponding ligands based on the 2,6-diformyl-4-methylphenol backbone. The present paper concentrates on the binuclear Cu(II) complexes **2**–**6** based on 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol backbones and featuring single-atom bridges (X = hydroxo, alkoxo, halo). In particular the crystal and molecular structure of compound **2a** is described as well as the detailed magnetic susceptibility properties of the species **2**–**6**. Major changes in magnetic behavior with subtle changes in the ligands are observed.[15a,b] In addition, the two mononuclear Cu(II) species **7** and **8**, in which the binucleating tendency of these ligands is not expressed, are discussed.



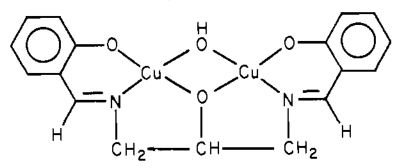
2a, X = OH, Y = ClO_4^- (+2H_2O)
b, X = Cl, Y = ClO_4^-
c, X = Br, Y = Br^-



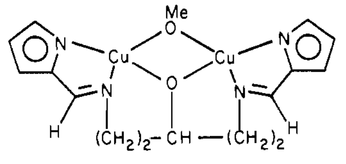
3a, Y = Cl^-, Z = PF_6^-
b, Y = Cl^-, Z = ClO_4^- (+1H_2O)



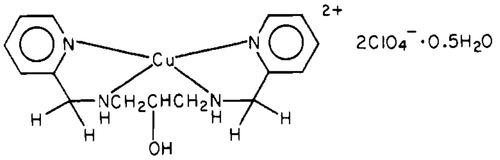
4a, X = Cl
b, X = OH
c, X = OEt



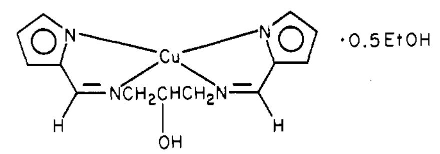
5



6



7



8

Experimental Section

Synthesis. Ligand Synthesis. The aldimine Schiff base ligands were formed by condensation of 2 equiv of pyridine-2-carboxaldehyde, pyrrole-2-carboxaldehyde, or salicylaldehyde with 1 equiv of commerically available 1,3-diaminopropan-2-ol (Aldrich Chemical Co. Ltd.) or with 1,5-diaminopentan-3-ol dihydrochloride which was prepared as follows: the dinitrile, 3-hydroxyglutaronitrile (4 g, 0.03 mol) was hydrogenated in a Parr hydrogenation vessel containing absolute ethanol (190 cm^3), concentrated hydrochloric acid (12 cm^3, 0.125 mol), and platinum oxide catalyst (0.2 g)[16] at room temperature at a pressure of 80 lb in.$^{-2}$ for 72 h. The resulting mixture was filtered,

---

(8) Grzybowski, J. J.; Merrell, P. H.; Urbach, F. L. *Inorg. Chem.* **1978**, *17*, 3078–3082.

(9) Gagne, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917–6927.

(10) Lontie, R. "Inorganic Biochemistry"; Eichhorn, G. I., Ed.; Elsevier: New York, 1973; p 344.

(11) Brown, J. M.; Powers, L.; Kincaid, B.; Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210–4216.

(12) (a) Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4217–4223. (b) Freedman, T. B.; Loehr, J. S.; Loehr, T. M. *Ibid.* **1976**, *98*, 2809–2815. (c) Co, M. S.; Hodgson, K. O.; Eccles, T.; Lontie, R. *Ibid.* **1981**, *103*, 984–986.

(13) (a) Himmelwright, R. S.; Eickman, N. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 1576–1586. (b) Himmelwright, R. S.; Eickman, N. C.; Lubien, C. D.; Solomon, E. I. *Ibid.* **1980**, *102*, 5378–5388.

(14) (a) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1–60. (b) "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley: New York, 1980.

(15) (a) A number of binuclear copper(II) complexes containing two-atom bridging from the pyrazolate and acetate ions and with the same ligand backbones have been prepared: Mazurek, W.; Berry, K. J.; Murray, K. S.; O'Connor, M. J.; Snow, M. R.; Rodgers, J. R.; Wedd, A. G., work in progress. (b) Some preliminary details of these bridged species have been presented: Berry, K. J.; Murray, K. S.; Mazurek, W.; O'Connor, M. J.; Wedd, A. G.; Snow, M. R. *Proc. Int. Conf. Coord. Chem., 21st* **1980**, 7. (c) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000–7001.

(16) Frampton, K. L.; Edwards, J. D., Jr.; Henze, H. R. *J. Am. Chem. Soc.* **1951**, *73*, 4432–4434.

and the volume of the filtrate was reduced to 40 cm^3 on a rotary evaporator. The solution was decanted and the white residue triturated with absolute ethanol (40 cm^3) until solid. The remaining solution was combined with the original decanted solution, and acetone (80 cm^3) was added to give additional white solid material. After filtration the solid was washed with acetone/ethanol and combined with the initially obtained product. Yield of product after drying in vacuo was 4.6 g (66%). The compound should be stored in a stoppered container to exclude moisture. Anal. Calcd for $C_5H_{16}N_2OCl_2$: C, 31.44, H, 8.88; N, 14.67; Cl, 37.13. Found: C, 31.43; H, 8.54; N, 14.33; Cl, 37.0. The ^{13}C NMR spectrum of this dihydrochloride in D_2O (0.4 g, 2 cm^3) measured relative to external tetramethylsilane gave resonance signals at 68.0 (C(3)), 37.8 (C(1)), and 34.4 (C(2)) ppm. An infrared spectrum (KBr disk) confirmed the absence of $\nu_{C\equiv N}$ (2250 cm^{-1}), which was present in the starting material.

1,5-Bis(salicylideneamino)pentan-3-ol. Potassium hydroxide (1.1 g, 0.02 mol) was dissolved in methanol (15 cm^3) and added to a solution of 1,5-diaminopentan-3-ol dihydrochloride (1.91 g, 0.01 mol) in methanol (25 cm^3). The mixture was filtered and added to salicylaldehyde (2.44 g, 0.02 mol). The yellow solution was allowed to evaporate in an open beaker overnight at room temperature to a volume of 20 cm^3. The resulting yellow crystalline Schiff base was filtered and washed with a little methanol (yield 1.7 g). An additional crop of crystals (0.6 g) was obtained by slow evaporation of the filtrate. Recrystallization from hot chloroform/methanol gave yellow needlelike crystals, mp 102–103 °C. Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.95; H, 6.74; N, 8.59. Found: C, 69.80; H, 6.57; N, 8.40.

The other ligands were synthesized in a similar manner. Only 1,5-bis(salicylideneamino)pentan-3-ol (vide supra) and 1,3-bis(salicylideneamino)propan-2-ol were isolated as solids. The others were prepared in situ and not isolated. When 1,5-diaminopentan-3-ol dihydrochloride was used, 2 equiv of KOH was added to the reaction mixture. The hydrogenated ligands were prepared in situ by reaction of methanolic solutions of the appropriate Schiff bases with sodium borohydride.

Preparation of Complexes. Compound 2a. Potassium hydroxide (2.24 g, 0.04 mol) in methanol (20 cm^3) was added to a solution of 1,5-diaminopentan-3-ol dihydrochloride (3.82 g, 0.02 mol) in methanol (50 cm^3). The mixture was filtered into freshly distilled pyridine-2-carboxaldehyde (4.28 g, 0.04 mol). After 0.3 h of warming the solution on a steam bath, it was evaporated to near dryness on a rotary evaporator. The residue was dissolved in chloroform (50 cm^3) and washed three times with water. The chloroform solution was dried over anhydrous magnesium sulfate. Filtration and volume reduction gave a brown oil (5.5 g) which was used in subsequent preparations.

The ligand (3 g, 0.01 mol) in ethanol (30 cm^3) was added to a stirred solution of cupric bromide hydrate (4.4 g, 0.02 mol) in ethanol (150 cm^3). The resulting mixture contained a brown precipitate and was stirred at 50 °C for 1.75 h and then at room temperature overnight. After filtration the brown solid was stirred with hot water (100 cm^3), and, after filtration, sodium perchlorate (5 g) in water (100 cm^3) was added to the green filtrate. Large green crystals formed over 2 days. Some light brown material which also formed was decanted off with excess solution, and the green crystals were collected, washed with water, and air-dried; yield 1.0 g. Anal. Calcd for $C_{17}H_{22}N_4O_{11}Cl_2Cu_2$: C, 31.12; H, 3.35; N, 8.54; Cl, 10.81; Cu, 19.37. Found: C, 31.13; H, 3.75; N, 8.37; Cl, 10.97; Cu, 19.22. (Note that the sample for microanalysis was dried in vacuo and 1 equiv of water is removed during this process to give the monohydrate.)

Compound 2b. The ligand (1.5 g, 0.005 mol) in ethanol (15 cm^3) was added to a stirred solution of cupric chloride dihydrate (1.7 g, 0.01 mol) in ethanol (50 cm^3) to give a green precipitate. The mixture was warmed on a steam bath for 1 h and cooled at room temperature before filtration. The bright green residue was washed with ethanol and dried under suction; yield 2.2 g. This material was dissolved in water (20 cm^3), and to this was added a solution containing sodium perchlorate (4 g) in water (30 cm^3). Green crystals formed on standing at room temperature, and after 1 week they were collected by filtration, washed with water, and air-dried; yield 1.1 g. Anal. Calcd for $C_{17}H_{19}N_4O_9Cl_3Cu_2$: C, 31.10; H, 2.89; N, 8.53; Cl, 16.20, Cu, 19.35. Found: C, 31.11; H, 2.81; N, 8.62; Cl, 16.24; Cu, 19.63.

Compound 2c. When a solution containing the ligand (0.3 g, 0.001 mol) in ethanol (30 cm^3) was added to a stirred solution of cupric bromide hydrate (0.44 g, 0.002 mol) in ethanol (30 cm^3), a thick brown precipitate formed. The mixture was warmed on a steam bath for 2 h, cooled, and filtered. The dark green residue (0.21 g) was dissolved in hot water (10 cm^3) and filtered hot and the filtrate allowed to evaporate at room temperature in an open beaker for several days. The mixture was filtered, and the green crystalline solid was washed with water and finally air-dried at room temperature; yield 0.17 g. Anal. Calcd for $C_{17}H_{19}N_4OBr_3Cu_2$: C, 30.84; H, 2.87; N, 8.46; O, 2.42; Br, 36.21; Cu, 19.20. Found: C, 30.77; H, 2.74; N, 8.32; O, 2.33; Br, 36.40; Cu, 19.82.

Compound 3a. The ligand (0.3 g, 0.001 mol) in warm methanol (30 cm^3) was reduced by addition of sodium borohydride (0.15 g, 0.004 mol) in small portions. The reaction mixture was refluxed for 10 min and then added dropwise to a solution of cupric chloride dihydrate (0.34 g, 0.002 mol) in methanol (10 cm^3) which was warmed on a steam bath for 1 h. The green mixture was filtered and the residue washed with methanol. To the combined filtrates was added Et_4NPF_6 (1 g, 0.0036 mol) in methanol (20 cm^3) and the solution allowed to stand overnight. The green platelike crystals that formed were collected, washed with methanol, and air-dried; yield 0.23 g. Anal. Calcd for $C_{17}H_{23}N_4Cl_2F_6N_4OPCu_2$: C, 31.80; H, 3.58; N, 8.72; Cl, 11.04; P, 4.82. Found: C, 31.62; H, 3.65; N, 8.56; Cl, 11.02; P, 4.73.

Compound 3b. The Schiff base ligand solution (3 g, 0.01 mol) in methanol (50 cm^3) was prepared and sodium borohydride (1.5 g, 0.04 mol) added over 30 min and the reaction mixture subsequently refluxed for 1 h. The mixture was evaporated to dryness in a rotary evaporator and chloroform (50 cm^3) added. The chloroform solution was washed with water (3 × 15 cm^3 portions), and after separation the chloroform layer was dried over anhydrous magnesium sulfate and filtered. Activated charcoal (0.5 g) was added to the filtrate which was heated on the steam bath for 15 min. The mixture was filtered and the filtrate evaporated to dryness to give a brown-yellow oil (1.6 g). The oil was dissolved in methanol (25 cm^3) and then added slowly to a stirred solution of cupric chloride dihydrate (1.7 g, 0.01 mol) in methanol (25 cm^3), giving an intense green color. A small amount of precipitate which formed dissolved when the mixture was heated on a steam bath for 1.5 h. Sodium perchlorate (2.5 g) in water (25 cm^3) was added and the mixture warmed on the steam bath. On cooling the green crystalline material which formed was collected by filtration, washed with water and ethanol, and air-dried; yield 1.15 g. Recrystallization from water/ethanol gave 0.69 g of pure product. Anal. Calcd for $C_{17}H_{25}N_4O_6Cl_3Cu_2$: C, 33.22; H, 4.07; N, 9.12; Cl, 17.30; Cu, 20.68. Found: C, 33.06; H, 4.17; N, 8.97; Cl, 17.2; Cu, 20.22.

Compound 4a. An ethanolic solution of the ligand (1.65 g, 0.005 mol) was added to a stirred solution of cupric chloride dihydrate (1.7 g, 0.01 mol) in ethanol in a total volume of 80 cm^3. Initially an olive green precipitate formed, but on complete addition of reactants and subsequent warming on a steam bath, the precipitate dissolved to give a deep green solution. Heating was continued for 0.75 h, and the solution was allowed to stand at room temperature for 3 h during which time a precipitate formed. The mixture was filtered, and the amorphous green residue was washed with water, ethanol, and ether; yield 0.65 g. The residue was then treated with chloroform (150 cm^3) in a Soxhlet extractor. The extract was filtered, and the deep green microcrystalline residue was washed with chloroform and dried under suction; yield 0.38 g. Anal. Calcd for $C_{19}H_{19}N_2ClCu_2$: C, 46.98; H, 3.91; N, 5.77; Cl, 7.30; Cu, 26.16. Found: C, 46.36; H, 3.88; N, 5.67; Cl, 7.9; Cu, 26.83.

Compounds 4b and 4c. A solution of the ligand (3.2 g, 0.01 mol) in ethanol (60 cm^3) was added dropwise to a stirred solution of cupric perchlorate hexahydrate (7.4 g, 0.02 mol) in ethanol (90 cm^3) to give a green solution. The apparent pH was adjusted to 11 with 10% aqueous sodium hydroxide. The mixture was filtered, and the green amorphous residue was washed with water and then ethanol and allowed to dry overnight at room temperature. The residue was then extracted with chloroform (120 cm^3) in a Soxhlet extractor over a period of 3 h. The chloroform extract was allowed to evaporate to near dryness at room temperature and was filtered and the green residue washed with chloroform and dried at room temperature; yield 0.34 g. The gray amorphous residue (3.5 g) from the extraction thimble was added to ethanol (50 cm^3), and the apparent pH was adjusted to 12.5 with aqueous sodium hydroxide solution and stirred overnight at room temperature, and then filtered and washed with ethanol. The now brown residue was again extracted with chloroform. The extract was filtered, yielding 0.14 g of a green microcrystalline solid, and a further 0.06 g was obtained by evaporation of the filtrate. The combined fractions were dissolved in hot chloroform (200 cm^3) and allowed to evaporate at room temperature to yield **4b** as a pale green microcrystalline solid (0.22 g). Anal. Calcd for $C_{19}H_{20}N_2O_4Cu_2$:

C, 48.84; H, 4.28; N, 5.99; Cu, 27.19. Found: C, 48.70; H, 4.25; N, 5.91; Cu, 27.68.

Extraction of the brown residue was continued for a further 2 days, and the brown-red extract was evaporated on a rotary evaporator to a volume of 50 cm^3, filtered, and washed with chloroform. A brown-red crystalline solid (1.28 g) was obtained. A further 0.19 g was obtained by the addition of ethanol to the filtrate and by allowing the chloroform to evaporate. The solid was recrystallized by dissolution in chloroform followed by addition of ethanol. Evaporation gave **4c**. Anal. Calcd for $C_{21}H_{24}N_2O_4Cu_2$: C, 50.92; H, 4.85; N, 5.66; Cu, 25.66. Found: C, 50.88; H, 4.79; N, 5.67; Cu, 26.13.

Compound 5. A solution of the ligand (1.5 g, 0.005 mol) in methanol (30 cm^3) was added to a stirred solution of cupric bromide hydrate (2.23 g, 0.01 mol) in methanol (50 cm^3), producing a brown suspension. Methanolic potassium hydroxide was added to an apparent pH of 13, giving a green solution which was warmed on a steam bath for 15 min. When the solution was cooled to room temperature, a green crystalline solid formed. The mixture was allowed to stand at room temperature for 3 h and filtered, and the solid material was washed with methanol and dried under suction; yield 2.4 g. Recrystallization of 2 g of the product from chloroform/methanol gave 1.5 g. Anal. Calcd for $C_{17}H_{18}N_2O_5Cu_2$: C, 44.65; H, 3.94; N, 6.13; Cu, 27.79. Found: C, 44.74; H, 3.93; N, 6.04; Cu, 26.41.

Compound 6. Potassium hydroxide (0.28 g, 0.005 mol) dissolved in a minimum volume of methanol was added to the ligand solution (0.48 g, 0.0025 mol) in methanol, giving a total volume of ca. 25 cm^3. The mixture was filtered, and pyrrole-2-carboxaldehyde (0.48 g, 0.005 mol) dissolved in methanol (10 cm^3) was added and the mixture was allowed to stand overnight at room temperature. The ligand solution was added to cupric chloride dihydrate (0.85 g, 0.005 mol) dissolved in methanol (25 cm^3) with stirring. The apparent pH was adjusted to 10. A dark olive green precipitate formed. The mixture was allowed to stand overnight at room temperature. The solvent was evaporated at room temperature, and the resulting residue was dissolved in a minimum of chloroform. The solution was filtered and then chromatographed on alumina (column diameter 1.2 cm; length 25 cm) and eluted with chloroform/toluene (1:1). The first red band (50 cm^3) was collected and evaporated to dryness, and the residue was redissolved in a minimum of chloroform; methanol, ca. one-third of the total volume, was added and the solution was allowed to evaporate in an open beaker at room temperature overnight. The red crystals obtained were filtered, washed with methanol, and then dried; yield 0.12 g. Anal. Calcd for $C_{16}H_{20}N_4O_2Cu_2$: C, 44.98; H, 4.68; N, 13.11; O, 7.49; Cu, 29.74. Found: C, 44.99; H, 4.67; N, 13.03; O, 7.52; Cu, 30.28.

Compound 7. A solution of pyridine-2-carboxaldehyde (10.7 g, 0.1 mol) in methanol (20 cm^3) was added to 1,3-diaminopropan-2-ol (4.5 g, 0.05 mol) dissolved in methanol (20 cm^3) and allowed to react overnight at room temperature. The volume was increased to 100 cm^3, and while the solution was warmed on a steam bath, sodium borohydride (3.8 g, 0.1 mol) was added in small quantities. The mixture was refluxed for 0.75 h and evaporated to dryness on a rotary evaporator. The solid was dissolved in chloroform (100 cm^3) and the solution washed three times with water (15 cm^3). The chloroform layer was separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated in vacuo to yield a yellow-brown oil (14 g).

This ligand (1.3 g, 0.005 mol) dissolved in ethanol (5 cm^3) was added slowly to a stirred solution of cupric chloride dihydrate (1.7 g, 0.01 mol) in ethhanol (50 cm^3) to give a green precipitate which was collected by filtration and then dissolved in water (35 cm^3), producing a deep blue color. Sodium perchlorate (4 g) dissolved in water (15 cm^3) was added. The mixture was warmed on a hot plate to dissolve some amorphous residue and then allowed to cool to room temperature. A total of 1.1 g of a crystalline solid was collected and recrystallized from water to give 0.26 g of a blue crystalline solid. Anal. Calcd for $C_{15}H_{21}N_4O_{9.5}Cl_2Cu$: C, 33.14; H, 3.86; N, 10.31; Cl, 13.04. Found: C, 33.14; H, 4.14; N, 10.39; Cl, 13.5.

Compound 8. Pyrrole-2-carboxaldehyde (1.9 g, 0.02 mol) was dissolved in ethanol (15 cm^3) and added to 1,3-diaminopropan-2-ol (0.9 g, 0.01 mol) in methanol (15 cm^3). The ligand mixture was warmed for 1 h before being added to cupric acetate tetrahydrate (4 g, 0.002 mol) dissolved in ethanol (230 cm^3). Red crystals began to form after a few minutes. The mixture was allowed to stand overnight at room temperature and then filtered to give 1.7 g of product after washing with ethanol and air-drying. Anal. Calcd for $C_{14}H_{17}N_4O_{1.5}Cu$: C, 51.15; H, 5.17; N, 17.04. Found: C, 50.91; H, 5.23; N, 17.17.

Table I. Crystal Data for **2a**

formula	$C_{17}H_{24}Cl_2Cu_2N_4O_{12}$	space group	*Pbca*
mol wt	674.4	a	27.287 (14) Å
ρ(obsd)	1.775 g/cm^3	b	12.000 (6) Å
ρ(calcd)	1.766 g/cm^3	c	15.487 (8) Å
μ(Mo Kα)	19.1 cm^{-1}	V	5071.1 $Å^3$
F(000)	2724	λ	0.7107 Å

Crystal Data for Title Compound 2a. The crystals were prepared from **2c** by recrystallization from water with added lithium perchlorate. The product was **2a** as confirmed by X-ray structure analysis.[17]

The crystals were shown to be orthorhombic, space group *Pbca*, by precession photography. A prism with dimensions 0.20 × 0.35 × 0.27 mm^3 was mounted about b and lightly coated with epoxy resin. The cell lengths at 21 °C were obtained from axial reflections by $\omega(h00, 00l)$ and $\mu(0k0)$ scans on a Stoe Weissenberg diffractometer using Mo Kα radiation and a graphite monochromator. The crystal data are given in Table I.

Intensity data were collected for the levels $h0l$ to $h,11,l$ in the range $0° < 2\theta < 45°$ with the ω-scan technique. Corrections for Lorentz and polarization effects were made but not for absorption to give 2202 nonzero structure factors with $I \geq 2.5\sigma I$.

Solution and Refinement of the Structure.[18] The structure was solved by a combination of direct and heavy-atom methods and refined by blocked-matrix least-squares techniques. All nonhydrogen atoms were treated anisotropically. Hydrogen atoms were placed in their calculated positions (C–H = 1.00 Å) except for those of the μ-OH group (H(22)) and of the water molecule (H(20), H(21)) coordinated to copper which were found in a difference map and refined with coupled temperature factors. The hydrogens of the lattice water molecule were not located. Individual layer scale factors were adjusted during the isotropic phase of the refinement when all atoms were placed. The weighting scheme was refined and converged at $w = 1.8/(\sigma^2(F) + 0.0031F^2)$. Final R was 0.0405 on F for 2202 nonzero reflections. The largest residuals in the final difference map were all less than 0.4e/Å.

All scattering factors (Cu^+ for Cu(II)) were taken from ref 19. A diagram of the cation is shown in Figure 1 and final atomic parameters (excluding calculated hydrogen atoms) are given in Table II. Tables III and IV contain the important molecular geometry. Anisotropic thermal parameters, least-squares planes, and atomic deviations from these planes, and the calculated hydrogen atom parameters have been deposited with a list of observed and calculated structure factors.

Magnetic Measurements. The magnetic susceptibilities of the solid complexes were determined over the temperature range 4.2–300 K with a Faraday balance. The detailed χ vs. T data have also been deposited as supplementary data. Plots of susceptibility or magnetic moment vs. temperature for selected examples are given in Figures 2–4. In the majority of cases the magnetic behavior conforms closely to the Bleaney–Bowers equation[20] for a spin-coupled $S = {}^1/_2$ system in which the triplet–singlet separation is $2J$. A negative value of J implies antiferromagnetic coupling (singlet-state lowest) while a positive value indicates ferromagnetism (triplet-state lowest). The observed data were fitted by least-squares methods to the Bleaney–Bowers equation allowing for the presence of monomer impurity.[21] The best fit values for g and J are given in Table V. In some cases a tetramer model was also used to fit the experimental data (Table VI) and further details are given in the Results and Discussion.

Spectral Measurements. Visible absorption spectra were measured on a Cary Model 17 spectrophotometer. Noise-decoupled C-13 NMR

---

(17) It was of some interest to also determine the crystal structure of **2c** because of its unusual magnetic properties discussed in this paper, but we have been unable to grow crystals which are not severely twinned. Although the title compound may be prepared by recrystallization of the latter compound in water with added $LiClO_4$, it may also be prepared directly as described in the Experimental Section.

(18) Program SHELX by G. M. Sheldrick, Cambridge, 1976.

(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(20) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451–465.

(21) Ginsberg, A. P. *Inorg. Chim. Acta. Rev.* **1971**, *5*, 45–68.

Table II. Fractional Coordinates (×10^4) for **2a**

atom	x	y	z
Cu(1)	968 (0)	5594 (1)	−537 (0)
Cu(2)	95 (0)	4238 (1)	−857 (0)
Cl(1)	−372 (1)	−3760 (1)	3450 (1)
Cl(2)	2440 (1)	−1436 (2)	2885 (1)
O(1)	770 (1)	4074 (3)	−569 (2)
O(2)	259 (1)	5783 (3)	−576 (2)
O(3)	−129 (2)	−2706 (4)	3356 (3)
O(4)	−171 (2)	−4327 (4)	4171 (3)
O(5)	−300 (2)	−4421 (4)	2697 (3)
O(6)	−877 (2)	−3591 (5)	3564 (4)
O(7)	−2170 (2)	2312 (6)	−3240 (5)
O(8)	−2728 (2)	1746 (7)	−2201 (5)
O(9)	2731 (2)	5928 (6)	−1493 (5)
O(10)	−2098 (3)	647 (7)	−2588 (6)
O(11)	1096 (1)	5756 (3)	−2022 (3)
O(12)	2204 (3)	1152 (8)	1379 (6)
N(1)	9 (2)	2689 (4)	−1238 (3)
N(2)	1645 (2)	5283 (4)	−182 (3)
N(3)	−562 (2)	4412 (3)	−1422 (3)
N(4)	1175 (2)	7152 (4)	−246 (3)
C(1)	−830 (2)	5342 (5)	−1537 (4)
C(2)	−1257 (2)	5337 (6)	−2020 (4)
C(3)	−1412 (3)	4357 (7)	−2382 (5)
C(4)	−1142 (3)	3407 (7)	−2273 (4)
C(5)	−713 (2)	3460 (5)	−1794 (4)
C(6)	−377 (2)	2535 (5)	−1658 (4)
C(7)	376 (3)	1828 (5)	−1135 (4)
C(8)	875 (3)	2246 (6)	−1215 (6)
C(9)	1079 (2)	3115 (5)	−639 (4)
C(10)	1603 (3)	3394 (7)	−725 (7)
C(11)	1868 (3)	4172 (6)	−212 (6)
C(12)	1879 (2)	6120 (6)	80 (4)
C(13)	1631 (2)	7188 (6)	81 (4)
C(14)	1831 (3)	8153 (6)	389 (5)
C(15)	1560 (4)	9109 (8)	343 (6)
C(16)	1101 (3)	9078 (6)	−8 (5)
C(17)	916 (2)	8078 (5)	−290 (4)
H(20)	1403 (22)	5752 (43)	−2193 (35)
H(21)	998 (21)	5276 (48)	−2195 (34)
H(22)	167 (19)	6197 (47)	−807 (34)

Table III. Bond Distances (Å) for **2a**^{a}

Cu(2)–N(1)	1.964 (4)	C(13)–C(14)	1.366 (11)
Cu(1)–N(2)	1.964 (5)	C(14)–C(15)	1.366 (13)
Cu(2)–N(3)	2.005 (4)	C(15)–C(16)	1.367 (13)
Cu(1)–N(4)	2.004 (4)	C(16)–C(17)	1.383 (10)
Cu(1)–O(1)	1.903 (3)	C(17)–N(4)	1.319 (8)
Cu(1)–O(2)	1.949 (3)	N(4)–C(13)	1.344 (7)
Cu(2)–O(1)	1.907 (4)	N(3)–C(5)	1.344 (7)
Cu(2)–O(2)	1.956 (3)	C(5)–C(4)	1.388 (9)
Cu(1)–O(11)	2.334 (4)	C(4)–C(3)	1.368 (11)
Cu(1)···Cu(2)	2.928 (1)	C(3)–C(2)	1.371 (11)
Cu(2)^{I}–O(5)	2.913 (5)	C(2)–C(1)	1.385 (8)
Cu(2)–O(2)^{II}	2.420 (4)	C(1)–N(3)	1.346 (7)
N(3)–C(5)	1.344 (7)	O(2)–H(22)	0.66 (6)
C(5)–C(6)	1.455 (9)	O(11)–H(21)	0.69 (6)
C(6)–N(1)	1.252 (7)	O(11)–H(20)	0.88 (6)
N(1)–C(7)	1.448 (8)	Cl(1)–O(3)	1.437 (5)
C(7)–C(8)	1.456 (11)	Cl(1)–O(4)	1.418 (5)
C(8)–C(9)	1.480 (10)	Cl(1)–O(5)	1.423 (4)
C(9)–O(1)	1.430 (7)	Cl(1)–O(6)	1.404 (6)
C(9)–C(10)	1.475 (10)	Cl(2)–O(7)	1.398 (4)
C(10)–C(11)	1.424 (12)	Cl(2)–O(8)	1.371 (6)
C(11)–N(2)	1.465 (9)	Cl(2)–O(9)	1.388 (6)
N(2)–C(12)	1.258 (8)	Cl(2)–O(10)	1.408 (5)
C(12)–C(13)	1.449 (10)		

^{a} Symmetry operations: (I) $-x, -y, -z$; (II) $-x, 1-y, -z$.

Table IV. Bond Angles (Deg) for **2a**

N(4)–Cu(1)–N(2)	81.3 (2)	N(1)–C(7)–C(8)	113.0 (6)
N(2)–Cu(1)–O(1)	95.3 (2)	N(1)–C(6)–C(5)	119.5 (5)
O(1)–Cu(1)–O(2)	80.2 (1)	C(6)–C(5)–N(3)	113.2 (5)
O(2)–Cu(1)–N(4)	100.3 (2)	Cu(2)–N(3)–C(5)	111.9 (4)
N(3)–Cu(2)–N(1)	82.0 (2)	Cu(2)–N(3)–C(1)	129.0 (4)
N(1)–Cu(2)–O(1)	95.0 (2)	C(1)–N(3)–C(5)	118.7 (5)
O(1)–Cu(2)–O(2)	79.9 (1)	N(3)–C(5)–C(4)	121.8 (6)
O(2)–Cu(2)–N(3)	101.7 (2)	C(5)–C(4)–C(3)	118.8 (7)
Cu(1)–O(2)–Cu(2)	97.1 (1)	C(4)–C(3)–C(2)	119.9 (7)
Cu(1)–O(1)–Cu(2)	100.4 (2)	C(3)–C(2)–C(1)	119.0 (6)
N(4)–C(13)–C(12)	113.8 (6)	C(2)–C(1)–N(3)	121.7 (6)
C(13)–C(12)–N(2)	118.0 (6)	Cu(1)–N(4)–C(13)	112.1 (4)
C(12)–N(2)–Cu(1)	114.6 (4)	Cu(1)–N(4)–C(17)	128.5 (4)
Cu(1)–N(2)–C(11)	123.7 (4)	C(13)–N(4)–C(17)	119.2 (5)
C(12)–N(2)–C(11)	121.8 (5)	N(4)–C(17)–C(16)	121.6 (6)
N(2)–C(11)–C(10)	113.8 (6)	C(17)–C(16)–C(15)	119.1 (7)
C(9)–C(10)–C(11)	126.3 (8)	C(16)–C(15)–C(14)	119.6 (8)
C(10)–C(9)–O(1)	113.2 (5)	C(15)–C(14)–C(13)	118.5 (7)
O(1)–C(9)–C(8)	113.1 (5)	C(14)–C(13)–N(4)	121.9 (6)
C(10)–C(9)–C(8)	118.0 (6)	Cu(1)–O(1)–C(9)	127.4 (3)
C(9)–C(8)–C(7)	122.9 (7)	Cu(2)–O(1)–C(9)	129.3 (3)
C(7)–N(1)–C(6)	122.2 (5)	Cu(1)–O(2)–H(22)	119 (5)
C(7)–N(1)–Cu(2)	124.0 (4)	Cu(2)–O(2)–H(22)	120 (5)
Cu(2)–N(1)–C(6)	113.4 (4)		

Table V. Magnetic Parameters for the Binuclear Compounds in the Solid State Based on a Dimer Model

compd	μ_{eff},^{c} μ_B	J,^{a} cm^{-1}	g	% monomer^b
2a	1.33	−142	1.98	1.6
2b	1.70	−15	1.96	9.1
2c	1.73			
3b	1.83	+80	2.03	0
4a	1.61	−53	1.95	0.2
4b	1.28	−148	1.90	0.4
4c	0.32	⩾−500		
5	1.70	+17	2.10	0.3
6	0.35	⩾−500		

^{a} Singlet–triplet splitting = $2J$ cm^{-1}, TIP contribution = 60 × 10^{-6} cgsu/Cu. ^{b} Estimated by fitting the magnetic data to a modified form of the Bleaney–Bowers equation.[21] ^{c} Per Cu atom, at 300 K.

Table VI. Magnetic Parameters Based on the Tetramer Model Shown in Figure 5

compd	J_{12}, cm^{-1}	J_{13}, cm^{-1}	J_{14}, cm^{-1}	g	% monomer
2a	−142	−2	26	2.02	1.6
2b	−15.9	−17.3	2.7	2.00	7.2
4a	−55	−37	13	2.00	0.2
4b	−151	−39	−48	2.00	0.4

spectra were recorded on a JEOL PS100 pulsed Fourier Transform spectrometer operating at 25.15 MHz.

Microanalyses were performed by Bernhardt Analytical Laboratories and the Australian Microanalytical Service.

Copper was determined by atomic absorption spectroscopy.

Results and Discussion

The diamines 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol readily react with salicylaldehyde, pyridine-2-carboxaldehyde, and pyrrole-2-carboxaldehyde to give ligands that are potentially pentadentate. The preparation of 1,5-diaminopentan-3-ol dihydrochloride was achieved in high yield by catalytic hydrogenation of 3-hydroxyglutaronitrile in *acidified* ethanol with a platinum catalyst. Reported methods for the reduction of dinitriles to the corresponding diamines are often complicated by the formation of five- and six-membered cyclized products especially in the presence of base.[22,23] The present synthesis avoids this problem.

Microanalytical data, the crystal structure of one of the compounds (**2a**) reported herein, and other properties described subsequently show that the hydroxyl group of the secondary

---

(22) Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York, 1967; p 217.

(23) Bowden, K.; Green, P. N. *J. Chem. Soc.* **1952**, 1164–1167.

Table VII. Electronic Absorption Spectral Data

	λ_{max} nm (ϵ, M^{-1} cm^{-1})						
compd	solid	$CHCl_3$	MeCN	DMF	MeOH	H_2O	Me_2SO
2a	620	*a*	605 (157)	600 (233)	*a*	620 (117)	622 (331)
2b	650	*a*	650 (174)	655 (213)	*a*	620 (87)	670 (179)
2c	760	*a*	*a*	710 (240)	675 (212)	610 (125)[b]	*a*
3b	660	*a*	675 (286)	693 (263)	640 (180)	595 (114)	*a*
4a	650	*a*	*a*	580 (187)	*a*	*a*	*a*
4b	620	572 (228)	*a*	*a*	*a*	*a*	*a*
4c	578	572 (245)	*a*	*a*	*a*	*a*	*a*
5	620	630 (214)	625 (184)	623 (366)	*a*	*a*	640 (225)
6	560	557 (267)	535 (203)	552 (269)	*a*	*a*	550 (195)
7	580	*a*	603 (158)	612 (390)	610 (132)	605 (135)	*a*
8	554	560 (113)	555 (97)	555 (104)	*a*	*a*	*a*

[a] Not measured. [b] On addition of $NaClO_4$ the spectrum of the aqueous solution changes rapidly to that of **2a**.

alcohol function is readily deprotonated in the presence of 2 equiv of copper(II) to give compounds in which the pentadentate ligand binds two copper ions. The exceptions are compounds **7** and **8**, which are mononuclear. The secondary hydroxyl group remains protonated in these cases and is apparently not coordinated as reported in several other compounds.[24,25] This is indicated by the infrared absorption spectra which show broad absorptions in the region of the OH stretching frequency at 3500 and 3300 cm^{-1}, respectively. In the present case both compounds involve the shorter chain ligand backbone derived from 1,3-diaminopropan-2-ol and pyrrole- or pyridine-2-carboxaldehyde. Apparently the steric strain in such cases with single-atom-bridging ligands, X, is too great for the formation of binuclear compounds.[26]

Figure 1 confirms the presence of a pentadentate, binucleating ligand in compound **2a**. The copper atoms are bridged by oxygen atoms O(1) and O(2) from the secondary alkoxo substituent of the ligand and the hydroxo group, respectively. The N_2O_2-donor-atom sets around each copper atom are essentially planar with Cu(1) and Cu(2) displaced by 0.179 and 0.126 Å, respectively, from the relevant N_2O_2 planes. The dihedral angle between the planes is 13.0°. Although Cu(1) and Cu(2) may be regarded as having "square-pyramidal" coordination and very similar "in-plane" coordination geometries, the nature of the apical ligand is very different for the two metal atoms. Cu(1) is bound to a H_2O ligand (O(11) at 2.234 Å) while Cu(2) has an interaction with O(2) of a neighboring binuclear unit at 2.420 Å as well as an additional weak interaction with a perchlorate oxygen at 2.913 Å. The structure thus involves *pairs of binucleated units*. The interactions leading to these *tetranuclear* units are similar to those present in the Cu(II) complex derived from the binucleating ligand 2,6-bis[[2-(4-imidazolyl)ethyl]imino]-methyl]-4-methylphenol.[27] In the present compound a second noncoordinated molecule of water is present in the lattice. The ligand backbone is under considerable angular strain as the angles at C(8), C(9), and C(10) are up to 14° above the normally observed values. The two Cu–O(1) bond lengths are 1.903 and 1.907 Å, the two Cu–O(2) bond lengths are 1.956 and 1.949 Å, and the intramolecular Cu(1)···Cu(2) distance is 2.928 Å while the angles Cu(1)–O(1)–Cu(2) and Cu(1)–O(2)–Cu(1) are 100.4 and 97.1°, respectively. Field desorption mass spectrometry[28] also suggests the presence of binuclear units. For example, the two ions of highest abundance in the mass spectrum of **2b** are the doubly charged ion $[Cu_2LCl]^{2+}$ and the "ion pair" $[Cu_2LCl(ClO_4)]^+$, where L is the relevant pentadentate ligand.

Table VIII. Molar Conductance of the Compounds in Various Solvents[a,b]

	Λ,[c] Ω^{-1} cm^2 mol^{-1}		
compd	CH_3OH	DMF	H_2O
2a	163	148	172
2b	175	139	286
2c	140	93	309
3b	151	69	432
7	181	365	201

[a] Concentration range (0.9–1.2) × 10^{-3} M. [b] The following ranges are expected for 1:2 electrolytes: for CH_3OH 160–220, for DMF 130–170, and for H_2O 235–273 Ω^{-1} cm^2 mol^{-1} for 10^{-3} M concentration.[35a,b] [c] Molar conductance.

A number of di-μ-hydroxo binuclear Cu(II) species have been structurally characterized,[5,29-33] and the relationship between the exchange parameter J and the Cu–O–Cu bond angles has been examined. The structural parameters of the present compound can be compared with the ranges observed in the di-μ-hydroxo species: Cu–O–Cu = 95–105°; Cu–μ-OH = 1.90–1.99 Å; Cu···Cu = 2.90–3.00 Å. A shorter Cu···Cu distance (2.78 Å) is observed for the "roof-shaped" structure described recently.[29,30,33] Some related compounds having a single μ-OH bridging group and with a considerably larger Cu–O–Cu bridging angle (132–143°) have been reported during the course of the present study.[34]

Physical Properties in Solution. Electronic spectral (Table VII) and conductance measurements (Table VIII) coupled with molecular weight determinations in solution suggest that compounds **2**–**6** can undergo significant structural changes upon dissolution and that the nature of that change is solvent dependent.

The binucleated species **2**–**6** all exhibit a broad electronic absorption band both in the solid state and in solution (Table VII). Previous investigations[2c,8] of species **1** assign similar absorptions to a d–d transition involving a Cu(II) atom bound

---

(24) Okamoto, M. S.; Barefield, E. K. *Inorg. Chem.* **1974**, *13*, 2611–2616.

(25) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1972**, *11*, 117–124.

(26) With potentially bridging groups such as the acetate and pyrazolate ions, complexes containing two copper centers have been prepared and characterized. In several cases triplet-state ESR spectra have been observed.[15a]

(27) Gagne, R. R.; McCool, M. W.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2420–2422.

(28) Cullis, P.; Derrick, P. J.; Wedd, A. G., unpublished observations.

(29) Charlot, M. F.; Kahn, O.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1410–1411.

(30) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Abaul, J.; Martin-Frere, J. *Inorg. Chem.* **1979**, *18*, 1675–1681.

(31) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110 and references therein.

(32) Mitchell, T. P.; Bernard, W. H.; Wasson, J. R. *Acta Crystallogr., Sect. B* **1970**, *B26*, 2096–2101.

(33) Itaka, Y.; Shimizu, K.; Kwan, T. *Acta Crystallogr.* **1966**, *20*, 803–811.

(34) (a) Haddad, M. S.; Wilson, W. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384–391. (b) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y.; Louis, R.; Weiss, R. *Ibid.* **1981**, *103*, 1273–1274. (c) Coughlin, P. K.; Lippard, S. J. *Ibid.* **1981**, *103*, 3228–3229.

either to an essentially planar four-coordinate coordination sphere or to five-coordinate pyramidal or six-coordinate pseudooctahedral coordination spheres involving "axial" solvent and/or intermolecular interactions. Compound **2a** is a 2:1 conductor[35a] in MeOH and DMF which indicates that the tetranuclear structural unit of the solid state dissociates to the component binuclear units in these solvents. The maximum of the electronic absorption band occurs at 620 nm in the solid and 600–622 nm in various solvents (Table VII) which suggests that the environment of the copper atoms is similar in the two phases. Equivalent observations obtain for **2b**. However, compound **2c** (X = Br) shows a considerable shift of electronic spectral maximum in solution up to 150 nm lower than that observed in the solid state (Table VII). Indeed, addition of $NaClO_4$ to an aqueous solution transforms the spectrum of **2c** to that of the hydroxo-bridged **2a**, and, in fact, **2a** can be recrystallized from such solutions (vide supra). In addition, solutions of **2c** show anomalously low molar conductances at 10^{-3} M in DMF and MeOH. While the molar conductances at 10^{-3} M of the species **3b** and **7** are in the range normally found for 2:1 electrolytes in MeOH, they exhibit anomalous values in DMF. In water, all compounds except **3b** exhibit molar conductances which might be ascribed[35b] to 2:1 electrolytes. The very high value found for **3b** may arise from hydrolytic processes similar to those thought to occur for related species.[2e]

The absorption spectra of chloroform solutions of the *neutral* species **4**, **6**, and **8** show a maximum in the range 550–580 nm, which is consistent[2e,36] with a planar coordination sphere for Cu(II) in this weakly donating solvent. The possible association of compound **4b** in the solid state (suggested by the absorption maximum of 620 nm) is not maintained in $CHCl_3$ solution (experimental molar mass: 552 ± 30 daltons vs. 467 calculated for the binuclear species). On the other hand, compound **5** is associated in $CHCl_3$ solution (1570 ± 120 daltons; 0.42–3.75 g/kg of $CHCl_3$ vs. 439 for the unassociated unit). Intermolecular association via Cu-bridging ligand interactions is an obvious possibility.

While the present solution physical data is incomplete (variation of spectral features, conductance, and molar mass with concentration is desirable), they serve to illustrate the structural lability of the present systems.

Magnetic Properties in the Solid State

(i) Fitting to Dimer and Tetramer Exchange Models. The susceptibility vs. temperature data for most of the complexes could be fitted extremely well to the Bleaney–Bowers equation for a binuclear $S = 1$ system. The fitting was carried out by using a least-squares procedure allowing for some, or all, of the parameters g, J, and percent monomer to vary. The results are given in Table V. The quality of fit was estimated by means of a discrepancy index $[\sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi_{obsd}^2]^{1/2}$. In a number of cases it can be seen that the g values are a little lower than 2.0 and hence outside the normal range of 2.0–2.2 expected from spin–orbit coupling considerations. We discuss below possible explanations for g being less than 2.0 but begin by assuming that the binuclear model represents the essential Cu–Cu interaction. Certainly the "intradimer" parameter is not altered significantly if "interdimer" interactions are included.

The hydroxo-bridged derivative **2a** shows a maximum in susceptibility at ca. 240 K which is typical of antiferromagnetic behavior (Figure 2, Table V). A J value of $-142\ cm^{-1}$ and $g = 1.98 \pm 0.02$ were obtained. The sharp increase in susceptibility at low temperatures is due to the presence of mononuclear species (1.6 mol %) which are commonly encoun-

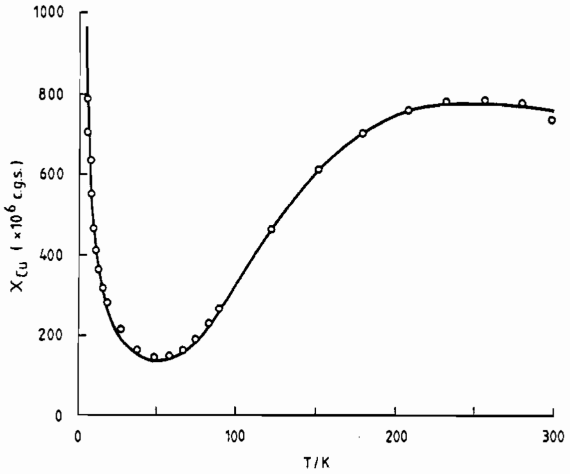


Figure 2. Temperature-dependent magnetic susceptibility (per Cu) of compound **2a**: (○) experimental data and (—) calculated curve from parameters in Table V.

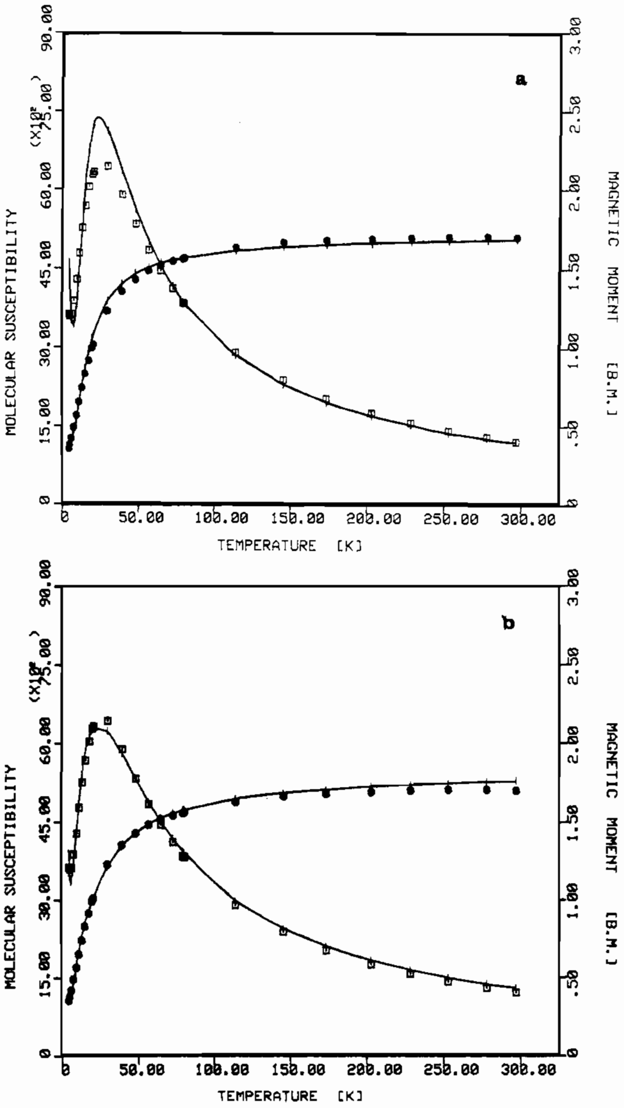


Figure 3. (a) Temperature-dependent magnetic susceptibility (□) and moment (●) (per Cu) of compound **2b** calculated with the dimer model and parameters in Table V. (b) Temperature-dependent magnetic susceptibility (□) and moment (●) (per Cu) of compound **2b**. The calculated curve is from the tetramer model and parameters in Table VI.

---

(35) (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122. (b) Angelici, R. J. "Synthesis and Technique in Inorganic Chemistry"; W. B. Saunders: London, 1977; p 213.

(36) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143–207.

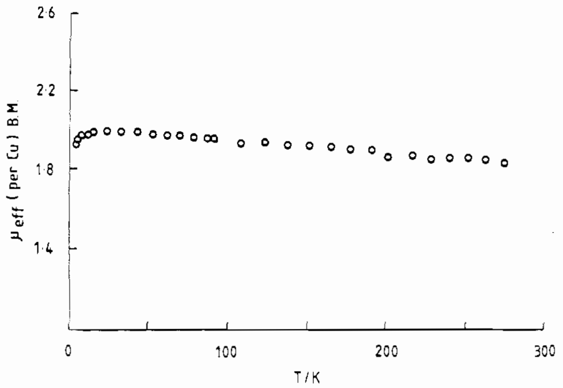


Figure 4. Magnetic moment vs. temperature plot for compound **3b**.

tered in such systems.[37] The chloro-bridged analogue **2b** shows a sharp maximum in susceptibility at 28 K with a corresponding J value of only -15 cm^{-1} (Figure 3). A larger concentration of monomer is evident by the leveling off of χ_{Cu} at very low temperatures at a value of ca. 3700×10^{-6} cgsu. The coupling is even weaker in the bromo-bridged derivative **2c** which displays Curie–Weiss behavior over the whole temperature range. The data could not be fitted to the Bleaney–Bowers equation even when using small values of J, and it is possible that exchange between Cu$_2$ units may be operative as was recently observed in some binuclear complexes.[38] We have so far been unsuccessful in growing crystals of **2c** suitable for X-ray analysis which would be useful in view of its anomalous magnetic, spectral, and conductance data.

Turning now to the chloro-bridged complex **3b**, in which the ligand imine functions of compound **2b** have been hydrogenated, fitting of the data shows that the sign of J is reversed (+80 cm^{-1}) from that observed for **2b**. Note that the stoichiometries of the two species differ by a water molecule and in the counter-anions. The temperature dependence of μ_{Cu} is shown in Figure 4. The moment increases gradually from 1.82 μ_B at 293 K to 2.00 μ_B at 24 K and then remains constant to ca. 7 K before decreasing to 1.93 μ_B at 4.3 K. This is the behavior expected for a ferromagnetically coupled $S = {}^1/_2$ pair in which only the $S' = 1$ level is populated below 24 K.[39] The small decrease in the moment below 7 K is probably due to antiferromagnetic intermolecular coupling, an effect observed in other binuclear systems,[30] or it may be due to zero-field splitting of the triplet state.

The salicylaldimine-based complexes **4a**–**4c** show weak antiferromagnetic coupling in the case of X = Cl (**4a**, $J = -53$ cm^{-1}), medium antiferromagnetic coupling for X = OH (**4b**, $J = -148$ cm^{-1}), and extremely strong antiferromagnetic coupling for X = OEt (**4c**), which is close to being diamagnetic at all temperatures. As in **2a** and **2b**, we note again that the best-fit g values are below 2.0 for **4a** and **4b**. With the shorter chain backbone ligand in compound **5**, ferromagnetism is again displayed ($J = +17$ cm^{-1}). Finally the pyrrole-2-carboxaldimine-based ligand in **6** forms a copper(II) complex having a bridging methoxo group and this compound is very strongly coupled and almost diamagnetic.

Before discussing the more general aspects of these magnetic results, we consider further the low g values deduced from the binuclear model for **2a**, **2b**, **4a**, and **4b**. There are a number of possible reasons for g being less than 2.0. One, of course, relates to the errors inherent in the present kind of fitting procedure, particularly where the low-temperature (where the effect of contaminating mononuclear species becomes significant) and high-temperature regions are being fitted simultaneously. The error in g is estimated to be ±0.02. Another is the possibility that the measured susceptibilities are consistently low on account of calibration errors. Neither of these explanations seems likely in view of the many concurrent measurements made with the same calibration constants and also since separate studies on other binuclear Cu(II) species yield "normal" g values. The most likely explanation is that the susceptibilities would be better described by a tetranuclear model rather than the binuclear model. The crystal structure shows that **2a** is made up of weakly linked binuclear units in which the Cu(1)–Cu(2) distance within each unit is 2.93 Å and the separation Cu(1)–Cu(3) between units is 3.1 Å. Calculations were therefore made by using a tetranuclear Hamiltonian similar to that developed by Hatfield and Inman[40] in describing the data for a Cu(II) tridentate Schiff base complex. The model is represented in Figure 5 and uses the assumption that J_{24} is zero. The number of variable parameters is, of course, increased compared to the binuclear model and we have taken great care, through a large number of least-squares fittings, to identify which are the most sensitive parameters. In the case of **2a** a good fit was obtained, equal to that deduced from the binuclear model as judged by the discrepancy index for the parameter values $g = 2.02$, $J_{12} = J_{34} = -142$ cm^{-1}, $J_{13} = -2$ cm^{-1}, and $J_{14} = J_{23} = -26$ cm^{-1}. The intradimer exchange interaction J_{12} is the same as in the binuclear model while the g value increases to a physically more reasonable value. Application of this tetramer model to complexes **2b**, **4a**, and **4b** likewise led to equivalent or improved fits compared to the dimer model, the best fit parameter values being given in Table VI. The improvement in the case of **2b** can be seen in Figure 3a,b where the tetramer model allows a better fit in the region of the susceptibility maximum. Some features of the exchange constant are worthy of note. In **2b** J_{13} is of similar magnitude to J_{12}. In this case if we assume that the binuclear units are associated in the solid state, then J_{13} will correspond to a double chloro-bridged pathway. J_{14} is weakly ferromagnetic in this and the related complex **4a** but antiferromagnetic in the μ-hydroxo species. The exchange pathways involve single ~90° Cu–Cl–Cu and Cu–O–Cu bridges, respectively. Finally we note that Boyd and Martin recently applied dimer and tetramer models to a chloro-bridged (dithiocarbamato)copper(II) complex in order

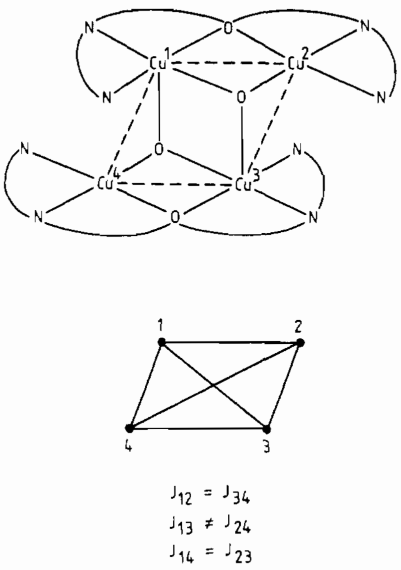


Figure 5. Schematic representation of the tetranuclear model for compound **2a** including labeling of the various J_{ij} constants.

---

(37) (a) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622–2630. (b) Berry, K. J.; Black, D. St. C.; Bos Van der Zalm, C. H.; Moss, G. I.; Murray, K. S. *Inorg. Chim. Acta* **1980**, *46*, 221–226.

(38) Swank, D. D.; Willett, R. R. *Inorg. Chem.* **1980**, *19*, 2321–2323.

(39) Wojciechowski, W. *Inorg. Chim. Acta* **1967**, *1*, 329–334.

(40) Hatfield, W. E.; Inman, G. W. *Inorg. Chem.* **1969**, *8*, 1376–1378.

to resolve a $g < 2$ problem of exactly the kind discussed here.[41] Their best fit g value was very similar to those given in Table VI.

(ii) General Discussion of Exchange Parameters. The compounds **3b** and **5** appear to be the first observed cases of net ferromagnetic coupling in this type of binucleated compound.[42] The previously reported examples exhibit net antiferromagnetic coupling with large negative values of J.[2,3,8] Ferromagnetism has been observed in some dimeric hydroxo-bridged copper(II) species of general type $[CuL_n(OH)]_2$[5] and in various *hetero* binuclear complexes (e.g., CuVO-$((fsa)_2en)$MeOH), the latter example displaying orthogonality of the magnetic orbitals on the two metal centers.[43]

The global parameter J, which contains an antiferromagnetic and a ferromagnetic contribution, provides little information concerning detailed exchange pathways. However, variation with what at first sight appear to be minor changes in ligand nature is striking. For example, the ligands in **4b** ($J = -148$ cm^{-1}) and **5** ($J = +17$ cm^{-1}) vary in the number of methylene groups in the backbone while the ligands in **3b** ($J = -15$ cm^{-1}) and **2b** ($J = +80$ cm^{-1}) vary in the degree of saturation at the imine function and also in the nature of anions present.

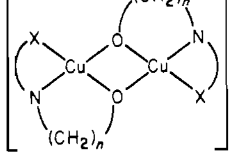
A fuller analysis will require detailed structural knowledge of an extended series of compounds followed by single-crystal magnetic studies in which the effects of systematic variation of geometric and other factors are determined. For the moment we can note that the presence of low point symmetry, the stereochemical lability of copper(II) (note the presence of H_2O in certain cases), and the presence of exchange interactions between Cu_2 units must be important influences.

Certain other points were worthy of note:

(1) The present systems follow the common observation in Cu(II) systems that chloro-bridged species display much weaker antiferromagnetic coupling than the corresponding hydroxo species.[2,3]

(2) The alkoxo-bridged species **4c** and **6** (which possess two alkoxo bridges) are very strongly coupled.

Similar strong antiferromagnetic coupling has led to diamagnetism in symmetric dialkoxo-bridged chelates of the type **9** studied by Curtis[44] and Martell.[45] In the case of $n = 3$, a six-membered chelate ring exists around Cu as it does in **4c** and **6**. The coupling was found to be much stronger than it was for $n = 2$ due, it was suggested, to the bridging O having close to trigonal geometry.[45,46] It is interesting to note that the angle Cu(1)–O(1)–O(9) (127.40°) in **2a** is similar to that observed in a $n = 3$ complex[44] and is likely to be similar in **4c** and **6**. A knowledge of geometries around the OMe and OEt groups in these compounds would be useful. Diamagnetism in binuclear Cu(II) complexes has now been observed in a variety of systems containing bridging groups such as azido,[47] triazenato,[48] hydroxo,[49] and alkoxo.[44,50] Clearly there are many factors which combine to give rise to overall diamagnetism. In the present limited study it is possible to tentatively conclude that the exogenous bridging group X needs to be alkoxide (or perhaps phenoxide) for a ligand backbone which contains an endogenous alkoxide bridge. This observation may be relevant to the nature of ligand and peptide-chain binding in type 3 copper enzymes and in hemocyanins which are thought to have binuclear coordination geometries related to those discussed here.[12,13]



9

(3) The reasons for net ferromagnetism occurring in **3b** and **5** should be more apparent when crystal structures become available. Hatfield, Hodgson, and co-workers[5] have shown that the sign of J is sensitive to small changes in the Cu–O–Cu bridging angle in symmetrical di-μ-hydroxo complexes of the type $(CuL_n(OH))_2$, while more recently Kahn et al.[29,30] have shown a dependence on the dihedral angle in related noncoplanar (roof-shaped) dimers. Kahn and Charlot[51] have discussed the relative contributions of antiferromagnetic (J_{AF}) and ferromagnetic (J_F) coupling in symmetrical binuclear species using the concepts of magnetic orbitals and overlap density between such orbitals in the vicinity of the bridging groups. Their calculations showed that J_{AF} and J_F were both sensitive to small changes in bridging angle and dihedral angle: J_F is less sensitive than J_{AF}. These geometric changes affect the size and magnitude of the overlap density around the bridging group which in turn leads to net antiferromagnetism or ferromagnetism. The present asymmetrically bridged compounds are more complicated to treat, but the basic principles of the Kahn model should still apply. The change in size of J in **4b** and **5** occurs as the methylene backbone varies in length. This structural difference presumably will lead to geometrical changes at the bridging groups. The variations between **3b** and **2b** involve differences in (a) saturation of the C–N linkage of the backbone, which will probably lead to geometric changes around Cu and perhaps even at the bridging group,[52] (b) the nature of the N-donor group in the backbone which can also influence the nature of the magnetic orbital and hence the overlap density, and (c) the presence of different anions may be important. If the present μ-hydroxo compounds follow a bridge-angle dependence of J similar to that shown by the symmetric di-μ-hydroxo complexes, it is likely that the two bridge angles in the ferromagnetically coupled species are less than that of compound **2a**.

It is very tempting to postulate that the present compounds possess two superexchange pathways (the backbone Cu–O–Cu path and the Cu–X–Cu path) which act in a semiindependent manner. The near-Curie behavior of the bromo-bridged **2c** might therefore result from accidental cancellation of antiferromagnetic and ferromagnetic contributions. Close scrutiny

---

(41) Boyd, P. D. W.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 105–108.

(42) Ferromagnetic coupling has also been observed with this type of ligand where the bridging group is the acetate anion. These compounds will be discussed in detail in a later publication.[15a]

(43) (a) Kahn, O.; Tola, P.; Galy, J.; Coudanne, H. *J. Am. Chem. Soc.* **1978**, *100*, 3931–3932. (b) Kahn, O.; Claude, R.; Coudanne, H. *Nouv. J. Chim.* **1980**, *4*, 167–172.

(44) Curtis, N. F.; Clark, G. R.; Skelton, B. W.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1977**, 1051–1055.

(45) Timmons, J. H.; Martin, J. W. C.; Martell, A. E.; Rudolf, P.; Clearfield, A.; Loeb, S. J.; Willis, C. J. *Inorg. Chem.* **1981**, *20*, 181–186.

(46) Barraclough, C. G.; Brookes, R. W.; Martin, R. L. *Aust. J. Chem.* **1974**, *27*, 1843–1850.

(47) Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381–3384.

(48) (a) Harris, C. M.; Hoskins, B. F.; Martin, R. L. *J. Chem. Soc.* **1959**, 3728–3736. (b) Corbett, M.; Hoskins, B. F.; McLeod, N. J.; O'Day, B. P. *Acta Crystallogr., Sect. A* **1972**, *A28*, 576–577.

(49) McFayden, W. D.; Robson, R. *J. Coord. Chem.* **1976**, *5*, 49–53.

(50) De Courcy, J. S.; Waters, J. N.; Curtis, N. F. *J. Chem. Soc., Chem. Commun.* **1977**, 572–573.

(51) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567–576.

(52) The X-ray structure of a complex related to **3b** of the type $Cu_2L_2Br_2$-(ClO_4) has been briefly described in ref 2e. It contains a saturated backbone with chelate ring sizes the same as in **3b**. Surprisingly it shows that one Br is bridging while the other is terminal. The two Cu environments are quite dissimilar, one being close to square pyramidal, the other nearer to trigonal bipyramidal. In principle this could lead to $[Cu(d_{x^2-y^2})/Cu(d_{z^2})]$ interactions and ferromagnetic coupling.[50] Robson et al.,[2e] however, observed antiferromagnetic coupling ($J = -70$ cm^{-1}) for their dibromo complex.

of Table V suggests that this is probably an oversimplification, and ongoing studies of a more extended series of compounds are required before more definite conclusions can be reached.[53]

Acknowledgment. We thank the Australian Research Grants Committee and the Monash University Special Research Grants (K.S.M.) for financial support. W.M. thanks the Public Service Board for the award of a Post Graduate Scholarship. We are grateful to Professor C. A. Reed for supplying a preprint of ref 15c.

Registry No. **2a**, 81554-46-3; **2b**, 81554-48-5; **2c**, 81554-49-6; **3a**, 81554-51-0; **3b**, 81600-77-3; **4a**, 81554-52-1; **4b**, 81554-53-2; **4c**, 81554-54-3; **5**, 81554-29-2; **6**, 81554-30-5; **7**, 81554-32-7; **8**, 81554-33-8; 1,5-bis(salicylideneamino)pentan-3-ol, 81555-05-7; 1,5-diaminopentan-3-ol, 81555-06-8; pyridine-2-carboxaldehyde, 1121-60-4; 1,3-diaminopropan-2-ol, 616-29-5; pyrrole-2-carboxaldehyde, 1003-29-8; salicylaldehyde, 69-72-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen atom parameters, least-squares planes, observed and calculated structure factors, and magnetic properties (24 pages). Ordering information is given on any current masthead page.

---

(53) For other recent discussions of net ferromagnetism in asymmetrically bridged Cu dimers see: Greenaway, A. M.; O'Connor, C. J.; Overman, J. W.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1508–1513.

Contribution from the Institut für Anorganische Chemie der Universität Basel, CH-4056 Basel, Switzerland,
Laboratoire de Chimie Minerale, Université Claude-Bernard, Villeurbanne Cedex, France,
Laboratoire de Cinétique et Génie Chimiques, INSA, Villeurbanne Cedex, France,
and Department of Chemistry, University of Southern California, Los Angeles, California 90007

Preparation and Molecular and Crystal Structure of *trans*-(*R*,*S*)-[Cr(2,3,2-tet)(NCS)$_2$]NCS

HELMUT R. MÄCKE,*[1a] BERNARD F. MENTZEN,[1b] JEAN PIERRE PUAUX,[1c] and ARTHUR W. ADAMSON[1d]

Received September 18, 1981

The complex [Cr(2,3,2-tet)(NCS)$_2$]NCS was prepared by a route expected to yield the cis form, namely, by stereoretentive substitution of thiocyanate for chloride in *cis*-Cr(2,3,2-tet)Cl$_2^+$. Crystal structure determination shows, however, that it is the trans isomer that actually is obtained. The structure determination was by X-ray single-crystal analysis. The thiocyanate complex crystallizes in the monoclinic $P2_1/c$ space group with a = 8.153 (2) Å, b = 15.556 (2) Å, c = 14.175 (2) Å, and β = 99.84 (2)°. There are four formula units per unit cell. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement led to a final value of the R (R_w) index of 0.0295 (0.0332) based on 2380 unique reflections. The chromium atom is hexacoordinated, and the six nitrogen atoms form a slightly distorted octahedron with a nearly planar CrN$_4$ unit. The use of visible and infrared spectroscopy for isomer identification is discussed for the case of thiocyanate-containing metal ammine complexes. Finally, the rate constant for thermal aquation of thiocyanate by aqueous Cr(2,3,2-tet)(NCS)$_2^+$ was found to be 6.4×10^{-8} s^{-1} at 53 °C.

Introduction

The crystal structure determination reported here was undertaken as the final resolution of an isomeric ambiguity that developed in the course of another investigation. We have been interested in the emission lifetimes from the first doublet thexi state, D_1^0, of Cr(III) complexes in aqueous solution.[2] Certain emission rules were proposed, as well as a possible correlation of lifetime, τ, with ground-state reactivity. The specific current study is one of the series CrN$_4$(NCS)$_2^+$ where N$_4$ denotes a tetradentate ligand, 2-ethylenediamine, or four ammonia ligands, and desired members of this series were *cis*- and *trans*-Cr(2,3,2-tet)(NCS)$_2^+$.

Since substitution reactins of chromium(III) ammines are generally isomer retentive,[3,4] it was assumed that replacement of chloride by thiocyanate in authentic *cis*-Cr(2,3,2-tet)Cl$_2^+$ would lead to the cis thiocyanato complex. The reaction proceeded cleanly; the product chromatographed as a single isomer, yet its emission lifetime was much longer than expected (26.4 μs in 20 °C aqueous solution).[5] The absorption spectrum (see Figure 1) showed resemblances to those of both *cis*- and *trans*-Cr(en)$_2$(NCS)$_2^+$. There is no splitting of the first ligand field or L$_1$ band, as often occurs with trans complexes, however.[6] The problem of siomer determination from spectra has been noted before in the case of thiocyanate complexes.[7,8]

Experimental Section

Materials. The ligand 2,3,2-tet (1,4,8,11-tetraazaundecane, H$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$) was obtained from Strem Chemicals, Inc., and CrCl$_3$·6H$_2$O from Riedel de Häen. *cis*-[Cr(2,3,2-tet)Cl$_2$]Cl·H$_2$O was synthesized following a literature procedure.[9] A 2.7-g sample of CrCl$_3$·6H$_2$O was dissolved in 50 mL of Me$_2$SO (dimethyl sulfoxide) and 1.6 g of 2,3,2-tet were added. The mixture was boiled for 30 min, followed by the addition of 150 cm^3 of acetone, which resulted in the precipitation of 2.5 g of a pink-violet solid. The product was washed with about 10 cm^3 of ice-cold methanol. About 150 mg of a light green solid, the color typical of a *trans*-dichloro chromium(III) ammine, was obtained on evaporation of the washings. This byproduct exhibited a three-band absorption spectrum and has been described earlier.[10] The spectrum of the main pink-violet product agreed as well with that in the literature,[9] and the analysis for chromium as CrO$_4^{2-}$, following basic perioxide oxidation,[11] gave 15.25 ± 0.15% of Cr, as compared to a calculated value of 15.42%.

[Cr(2,3,2-tet)(NCS)$_2$]NCS. A 1.4-g sample of the *cis*-dichloro compound above was dissolved in 40 cm^3 of water, and 1.5 g of sodium thiocyanate was added. The mixture was heated, at 90 °C for 4 h, with stirring. On cooling to room temperature a clean appearing crop of orange-red crystals was obtained, which was washed with 10 cm^3 of cold water to give a yield of 1.45 g or 85%. Anal. Calcd for

---

(1) (a) Universität Basel. (b) Université Claude-Bernard. (c) INSA. (d) University of Southern California.

(2) See: Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53.

(3) Garner, C. S.; House, D. A. *Transition Met. Chem.* **1970**, *6*, 200.

(4) Couldwell, M. C.; House, D. A. *Inorg. Chem.* **1972**, *11*, 2024.

(5) Mäcke, H. R.; Adamson, A. W., unpublished work.

(6) Perumareddi, J. R. *Coord. Chem. Rev.* **1969**, *4*, 73.

(7) Poon, C. K.; Pun, K. C. *Inorg. Chem.* **1980**, *19*, 568.

(8) Zinato, E.; Riccieri, P. *Inorg. Chem.* **1973**, *12*, 1451.

(9) Bosnich, B.; Gillard, R. D.; McKenzie, E. D.; Webb, G. A. *J. Chem. Soc. A* **1966**, 1331.

(10) Kutal, C.; Adamson, A. W. *Inorg. Chem.* **1973**, *12*, 1990.

(11) Haupt, G. *J. Res. Nat. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.

0020-1669/82/1321-3080$01.25/0