Binuclear Copper(II) Complexes of 1,4,7-Trimethyl-1,4,7-triazacyclononane: Synthesis, Spectroscopy, and Spin Coupling across Multiple-atom Bridges of Variable Length (3.6—7.6 Å)

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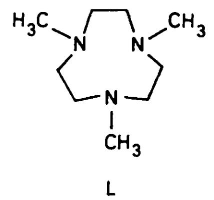
Thirteen new binuclear copper(II) complexes $[LCu(\mu\text{-}X)CuL]^{2+}$ with L = 1,4,7-trimethyl-1,4,7-triazacyclononane and X = $2Cl^-$, $2Br^-$, $2SCN^-$, $C_2O_4^{2-}$, $(HN)_2C_2O_2^{2-}$, $Cl_2C_6O_4^{2-}$, $H_2C_6O_4^{2-}$, and $2CH_3CO_2^-$ have been synthesized and characterized based on i.r., electronic, and e.s.r. spectroscopy and variable-temperature (100—300 K) magnetic susceptibility measurements. A varying range of magnetic interactions, no coupling, antiferromagnetic ($2J = -460$ cm^{-1}), and ferromagnetic ($J = +22$ cm^{-1}) coupling, has been observed between the copper(II) ions in these binuclear systems with variable metal–metal separation estimated to be in the range of 3.6—7.6 Å. The interaction is more effective through a μ-oxamato bridge ($2J = -460$ cm^{-1}) than through a μ-oxalato bridge ($2J = -300$ cm^{-1}). A moderately strong antiferromagnetic interaction ($2J = -60$ cm^{-1}) has been found for the $Cl_2C_6O_4^{2-}$-bridged compound, where the Cu ··· Cu separation is expected to be ≈7.6 Å. The *X*-band e.s.r. spectra of the polycrystalline substances at 120 K indicate square-pyramidal geometry for the copper with a $(d_{x^2-y^2})^1$ ground state. A mixed bridged compound (μ-1,1-N_3)(μ-OH), with a ferromagnetic interaction between the copper centres is also described. The difference in magnetic exchange interaction between the different copper(II) systems is discussed.

The study of binuclear copper(II) complexes is a topic of considerable current interest,[1] because of their use as models for a number of important biological systems containing a coupled binuclear copper active site.[2] The focus of much of this work has been on magnetic exchange interactions[3] between the two copper(II) ions, which may be diagnostic for the nature and geometry of the ligand-bridged binuclear centre. These efforts have resulted in a better fundamental understanding of spin exchange through multiatomic bridges[4] and in the synthesis of models for biological polynuclear active centres and of molecular materials exhibiting new but predictable magnetic properties.[3b]

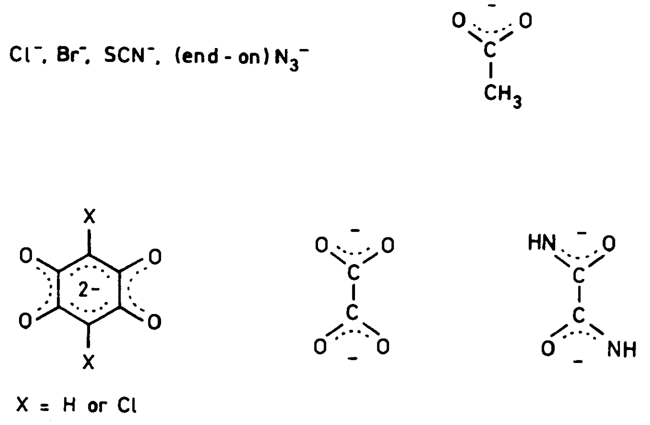
In the last few years we have been investigating the ligating properties of the small tridentate cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (L) towards substitution-labile first-transition-series[5] bivalent metal ions. This ligand co-ordinates facially with one nitrogen in the apical position and prevents for steric reasons the formation of ML_2 moieties; only one ligand per metal centre can be bound. Thus, in the presence of bridging ligands, stable complexes containing a dimetal core are readily obtainable. These materials are ideally suited for the study of intramolecular magnetic exchange interactions.



L

Our continuing interest in copper chemistry led us to study new binuclear copper(II) complexes with L. Previously reported structural data for copper(II) complexes[6] with this ligand revealed them to be binuclear and five-co-ordinate cations; in this work we present data to support the generality of the five-co-ordination and the binuclear nature of the complexes with this macrocyclic N-donor ligand. This ligand prefers to impose a square-based pyramidal geometry around copper(II) ions and hence a $(d_{x^2-y^2})^1$ ground state.

Several authors have sought to establish various criteria for judging the viability of a particular single-atom[7] or polyatomic bridging[3b,7,8] unit to support a magnetic exchange interaction between two paramagnetic metal ions. Much of this work has been concerned with exchange interactions in binuclear or dimeric copper(II) complexes and has indicated that the strength of the exchange interaction depends primarily upon the symmetry and energy of the copper(II) ground state relative to the highest occupied molecular orbitals of the bridging moiety. In an effort to vary the length of the bridging unit and still maintain an exchange interaction between the copper(II) ions, we report in this paper CuL^{2+} complexes bridged by the following anions. Furthermore, we have attempted to verify the requirements (see below), which emerged mainly from the work of Hendrickson *et al.* and Kahn *et al.*, concerning the possibility



of maximizing the interaction between two copper ions separated by a distance in the range of 4—8 Å.

Experimental

The ligand 1,4,7-trimethyl-1,4,7-triazacyclononane ($C_9H_{21}N_3$, L) was prepared by a procedure described elsewhere.[9] All other starting materials were commercially available and of reagent grade. Elemental analyses were performed by Beller Microanalytical laboratory, Göttingen and by Microanalytical Laboratory, Ruhr-University, Bochum. Copper was determined gravimetrically by using *N*-benzyl-*N*-phenylhydroxylamine. The perchlorate anion was determined gravimetrically as tetraphenylarsonium(v) perchlorate. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer in solution using methanol or acetonitrile as solvent. The positions of the absorption maxima were checked by measuring the reflectance spectra (KBr disks) of the respective solid in order to ensure the identity of the species in solution and in the solid state. Infrared spectra were taken as KBr pellets on a Beckman Acculab 10 IR or Perkin-Elmer 1720X FT-IR spectrometer. Variable-temperature susceptibility measurements were made between 100 and 298 K by using the Faraday method. The magnetic data were corrected for the diamagnetism of the bucket at each temperature, and then for the diamagnetism of the ligands by using Pascal's constants. E.s.r. spectra of the synthesized dicopper complexes were obtained for the undiluted polycrystalline solids between 120 and 293 K using a Varian E-9 *X*-band e.s.r. spectrometer equipped with a Varian variable-temperature controller and a Nicolet 1070 Instrument computer.

$[Cu_2L_2(\mu\text{-}SCN)_2][SCN]_2$ (**1**).—To a suspension of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.4 g) in methanol (20 cm^3) was added a 1 mol dm^{-3} methanolic solution (2 cm^3) of 1,4,7-trimethyl-1,4,7-triazacyclononane at room temperature with stirring. Then a methanolic solution (20 cm^3) of NaSCN (0.16 g) was added. The green solution was allowed to stand at ambient temperature for 24 h, during which time green crystals precipitated. These were filtered off and air-dried. Yield: 0.76 g, 54%.

$[Cu_2L_2(\mu\text{-}SCN)_2][ClO_4]_2$ (**2**).—A 1 mol dm^{-3} methanolic solution (1 cm^3) of the macrocyclic amine ligand was added to a stirred methanolic solution (20 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g) at room temperature. Sodium thiocyanate (0.08 g) dissolved in methanol (20 cm^3) was added to the resulting blue solution. After 3—4 h at 5 °C needle-shaped, green crystals separated, which were filtered off and air-dried. Yield: 0.44 g, 56%.

$[Cu_2L_2(\mu\text{-}Cl)_2][ClO_4]_2$ (**3**).—To $CuCl_2 \cdot 2H_2O$ (0.34 g) dissolved in methanol (30 cm^3) was added a 1 mol dm^{-3} methanolic solution (2 cm^3) of L with stirring at room temperature. A solution of $NaClO_4 \cdot H_2O$ (0.48 g) in methanol (20 cm^3) was added. This solution, kept at 20 °C in an open beaker, provided green crystals, which were filtered off and air-dried. Yield: 0.65 g, 44%. Complex (**3**) was also obtained in an analogous manner by using $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol), the amine (1 mmol), and NaCl (4 mmol).

$[Cu_2L_2(\mu\text{-}Cl)_2]Cl_2 \cdot 2H_2O$ (**4**).—To a solution of $CuCl_2 \cdot 2H_2O$ (0.17 g) in methanol (20 cm^3) was added a 1 mol dm^{-3} methanolic solution (1 cm^3) of L. After 4—5 d at 5 °C, green crystals precipitated, which were filtered off and air-dried. Yield: 0.19 g, 30%.

$[Cu_2L_2(\mu\text{-}Cl)Cl_2]ClO_4$ (**5**).—A 1 mol dm^{-3} methanolic solution (1 cm^3) of L was added to a stirred solution of $CuCl_2 \cdot 2H_2O$ (0.17 g) in acetonitrile or isopropyl alcohol. Then $NaClO_4$ (0.12 g) was added and stirring was continued for 15 min. The solution was allowed to stand at 5 °C for 3 h, during which time an olive-green solid precipitated; recrystallization of the solid yielded olive-green microcrystals. Yield: 0.39 g, 58%.

$[Cu_2L_2(\mu\text{-}Br)Br_2]ClO_4$ (**6**).—Ochre crystals were obtained by using a solution of $CuBr_2$ in methanol in a similar way as for complex (**5**). Yield: 0.38 g, 47%.

$[Cu_2L_2(\mu\text{-}Br)_2]Br_2 \cdot 2H_2O$ (**7**).—Brown crystals were obtained in a similar way as for (**4**) but using $CuBr_2$. Yield: 0.37 g, 47%.

$[Cu_2L_2(\mu\text{-}O_2CCH_3)_2][PF_6]_2$ (**8**).—To a suspension of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.20 g) in methanol (30 cm^3) was added a 1 mol dm^{-3} methanolic solution of L (2 cm^3) with vigorous stirring to obtain a deep blue solution. Solid sodium hexafluorophosphate (0.30 g) was added. Turquoise green crystals were obtained after 2 d at 20 °C. They were filtered off and air-dried. Yield: 0.46 g, 52%.

$[Cu_2L_2(\mu\text{-}C_2O_4)][ClO_4]_2$ (**9**).—A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.93 g) in water (20 cm^3) was treated with a 1 mol dm^{-3} methanolic solution (2.5 cm^3) of L. On addition of oxalic acid (0.63 g) in water (20 cm^3) to the resulting blue solution a white solid precipitated. The suspension was treated dropwise with a 1 mol dm^{-3} sodium hydroxide solution with vigorous stirring until a clear solution was obtained. This was kept in an open vessel for 12 h and then treated with enough ethanol to produce a turbidity. The solid was filtered off and turquoise blue crystals were obtained from the filtrate on keeping it in an open vessel at 20 °C. They were collected and air-dried. Yield: 0.66 g, 35%.

$[Cu_2L'_2(\mu\text{-}C_2O_4)][ClO_4]_2$ (**14**).—This was prepared in a similar way as for (**9**) using 1,4,7-triazacyclononane (L′) instead of the permethylated cyclic amine. Blue crystals. Yield: 65%.

Alternatively, a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.55 g) and a 1 mol dm^{-3} methanolic solution (1.5 cm^3) of the cyclic amine (L or L′) in methanol (25 cm^3) was treated with an aqueous solution (20 cm^3) of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (0.175 g). The solution was stirred vigorously for 15 min, during which time a white solid, $KClO_4$, precipitated. The solid was filtered off and the clear blue solution cooled at 5 °C overnight, when deep blue crystals of complex (**9**) or light blue crystals of (**14**) appeared. They were collected and air-dried. Yield: 70—80%.

$[Cu_2L_2(\mu\text{-}Cl_2C_6O_4)][ClO_4]_2$ (**10**).—Chloroanilic acid (2,5-dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione) (0.1 g) was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g) and L (0.175 g) in methanol (60 cm^3) with vigorous stirring. The stirring was continued for 15 min. Then solid sodium perchlorate (0.12 g) was added and the solution kept in a beaker at 20 °C for 24 h. Slow evaporation afforded black needle-shaped crystals, which were filtered off and air-dried. Yield: 0.46 g, 52%.

$[Cu_2L_2(\mu\text{-}H_2C_6H_4)][ClO_4]_2$ (**11**).—In an analogous way, using 2,5-dihydroxybenzoquinone instead of chloranilic acid, brown crystals of (**11**) were obtained. Yield: 0.49, 61%.

$[Cu_2L_2\{\mu\text{-}(NH)_2C_2O_2\}][B(C_6H_5)_4]_2$ (**12**).—Oxamide (0.05 g) was suspended in acetone (15 cm^3) and treated with NaOH (0.07 g) with vigorous stirring to obtain a clear solution. To this solution was added with stirring a solution of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.2 g) and L (0.172 g) in acetone (15 cm^3). Sodium tetraphenylborate (0.34 g) in acetone (25 cm^3) was added after 15 min to obtain a green solid, which was recrystallized from

Table 1. Analytical and selected i.r. spectral data (vs = very strong; s = strong; m = medium; w = weak)

Compound	Analysis[a]/%						I.r.[b]/cm^{-1}
	C	H	N	ClO_4	Cl/Br	Cu	
(1) $[Cu_2L_2(SCN)_2][SCN]_2$	37.45	6.00	20.50			18.10	ν(CN) 2 100, 2 050vs
	(37.65)	(6.05)	(19.95)			(18.10)	
(2) $[Cu_2L_2(SCN)_2][ClO_4]_2$	31.05	5.05	14.70	25.20		16.60	ν(CN) 2 100
	(30.60)	(5.40)	(14.30)	(25.35)		(16.20)	
(3) $[Cu_2L_2Cl_2][ClO_4]_2$	29.30	5.85	11.25	27.20	9.30	17.90	
	(29.25)	(5.70)	(11.35)	(26.90)	(9.60)	(17.20)	
(4) $[Cu_2L_2Cl_2]Cl_2{\cdot}2H_2O$	33.10	7.10	13.00		21.60	19.50	ν(OH) 3 360m, 1 610w
	(33.40)	(7.15)	(13.00)		(21.90)	(19.65)	
(5) $[Cu_2L_2Cl_3][ClO_4]$	32.40	6.25	12.50	14.70	16.20	19.10	
	(32.00)	(6.25)	(12.45)	(14.70)	(15.75)	(18.80)	
(6) $[Cu_2L_2Br_3][ClO_4]$	27.65	5.30	10.45	12.80	29.50	16.00	
	(26.75)	(5.25)	(10.40)	(12.30)	(29.65)	(15.70)	
(7) $[Cu_2L_2Br_2]Br_2{\cdot}2H_2O$	26.40	5.70	10.25		38.90	15.20	ν(OH) 3 400m, 1 600w
	(26.20)	(5.60)	(10.20)		(38.75)	(15.45)	
(8) $[Cu_2L_2(CH_3CO_2)_2][PF_6]_2$	29.40	5.50	9.65			14.25	ν(CO) 1 581s, 1 429m, 730w
	(30.10)	(5.50)	(9.60)			(14.50)	ν(PF_6) 820s, 545m
(9) $[Cu_2L_2(C_2O_4)][ClO_4]_2$	31.30	5.80	11.00	26.20		16.70	ν(CO) 1 630s, 1 355m, 730w
	(31.40)	(5.60)	(11.10)	(26.30)		(16.80)	
(10) $[Cu_2L_2(Cl_2C_6O_4)][ClO_4]_2$	32.60	4.90	9.70	22.90	7.90	14.20	ν(CO) 1 510s, 740w
	(32.95)	(4.85)	(9.60)	(22.70)	(8.10)	(14.50)	
(11) $[Cu_2L_2(H_2C_6O_4)][ClO_4]_2$	35.35	5.35	10.65	24.65		15.75	ν(CO) 1 520s, 725w
	(35.75)	(5.50)	(10.40)	(24.65)		(15.75)	
(12) $[Cu_2L_2\{(HN)_2C_2O_2\}][B(C_6H_5)_4]_2$	69.30	7.20	9.60			10.50	ν(NH) 3 300m, ν(CO) 1 605s, 1 565m, 770m, ν(BC) 730, 720, 700s
	(68.40)	(7.10)	(9.40)			(10.65)	
(13) $[Cu_2L_2(N_3)(OH)][ClO_4]_2$	29.60	5.90	17.35	28.00		17.35	ν(N_3) 2 050s, ν(OH) 3 450m
	(29.70)	(5.95)	(17.35)	(27.35)		(17.45)	
(14) $[Cu_2L'_2(C_2O_4)][ClO_4]_2$	25.60	4.40	12.30	29.80		18.50	ν(CO) 1 655s, 1 340m, 760w
	(25.00)	(4.50)	(12.50)	(29.60)		(18.90)	

[a] Calculated values in parentheses. Given chlorine percentage = (total chlorine content − chlorine content in perchlorate ion). [b] As KBr pellets. Two bands in the ranges 1 100—1 075s and 620—605m cm^{-1} for all perchlorate-containing complexes.

acetonitrile. The green crystals were collected and air-dried. Yield: 0.57 g, 48%. Instead of acetone, acetonitrile could also be used as solvent.

$[Cu_2L_2(\mu\text{-}N_3)(\mu\text{-}OH)][ClO_4]_2$ (**13**).—To an aqueous solution (50 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.37 g) and a 1 mol dm^{-3} methanolic solution (1 cm^3) of L was added dropwise NaN_3 (0.03 g) dissolved in water (20 cm^3) with constant stirring at room temperature. The green solution when subjected to slow evaporation at room temperature afforded deep green crystals after 4 d. They were filtered off and air-dried. Yield: 0.33 g, 45%.

CAUTION: Although we experienced no difficulties with the compounds isolated as their perchlorate salts, the unpredictable behaviour of perchlorate salts necessitates extreme caution in their handling.

Results and Discussion

The evidence for the binuclear nature of the complexes comes from the stoicheiometry, i.r., electronic, and e.s.r. spectra, and magnetic susceptibility measurements.

Syntheses of the Complexes.—Analytical data (Table 1) indicate that the macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L) forms a very stable 1 : 1 complex with copper(II) ions in different solvents, which forms a series of binuclear bridged complexes $[Cu_2L_2X]^{2+}$, where X = $2Cl^-$, $2Br^-$, $2SCN^-$, $2CH_3CO_2^-$, chloroanilate^{2-}, oxalate^{2-}, oxamidate^{2-}, *etc.*, in the presence of different bridging ligands. In the presence of perchlorate and chloride anions olive-green crystals of (**5**) are formed in acetonitrile or Pr^{i}OH at 5 °C within 3 h. At higher perchlorate concentrations a different product was obtained as deep green crystals (**3**), from a methanolic solution. With $CuCl_2{\cdot}2H_2O$ as the starting material in the absence of ClO_4^- anions under otherwise identical conditions, green crystals of (**4**) were obtained, which is the dichloride salt of the cation $[Cu_2L_2(\mu\text{-}Cl)_2]^{2+}$, present also in complex (**3**). The same type of reactions using copper acetate as starting material in presence of thiocyanate afforded di-μ-thiocyanato-dicopper(II) complexes (**1**) and (**2**).

The reaction of $[Cu_2(CH_3CO_2)_4]{\cdot}2H_2O$ with the macrocyclic amine ligand afforded, only in the presence of hexafluorophosphate as anion, the di-μ-acetato-dicopper unit, (**8**). In the presence of perchlorate anions the previously reported di-μ-hydroxo complex[6a] was obtained under otherwise identical conditions.

Addition of a soluble oxalate to a methanolic solution of $Cu(ClO_4)_2{\cdot}6H_2O$ and the amine ligands afforded crystals of compositions $CuL(0.5C_2O_4)(ClO_4)$ (**9**) or $CuL'(0.5C_2O_4)(ClO_4)$ (**14**). Interestingly, these complexes were also synthesized by electrophilic attack of aminecopper(II) ion on the co-ordinated oxalate ligands in tris(oxalato)chromate(III) ion. Mechanistic studies of this type of metal-assisted aquation of tris(oxalato)chromate(III) ion have been reported.[10] In line with these studies, the reaction scheme shown below can be envisaged for the formation of μ-oxalato complexes (**9**) and (**14**). To increase the intramolecular distances between two copper atoms, hydranilic (2,5-dihydroxycyclohexa-2,5-diene-1,4-dione) and chloranilic acids were used as bridging coligands; the syntheses of complexes (**10**) and (**11**) were achieved very similarly to those described above. It is noteworthy that the μ-oxamidato compound (**12**) could only be obtained as its tetraphenylborate salt. Compound (**13**) with mixed bridges, $[Cu_2L_2(N_3)(OH)][ClO_4]_2$, was obtained by treating the di-μ-hydroxo-dicopper(II)

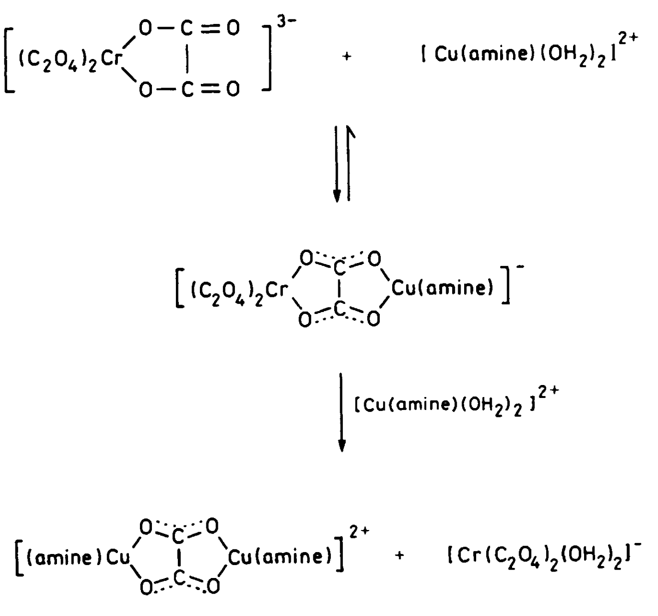


Table 2. Electronic spectra * for binuclear copper(II) complexes

Complex	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
(**1**) $[Cu_2L_2(SCN)_2][SCN]_2$	637 (544), 1 066 (111)
(**2**) $[Cu_2L_2(SCN)_2][ClO_4]_2$	638 (205), 1 069 (42)
(**3**) $[Cu_2L_2Cl_2][ClO_4]_2$	669 (121), 1 178 (46)
(**4**) $[Cu_2L_2Cl_2]Cl_2{\cdot}2H_2O$	460 (553), 712 (121), 1 175 (42)
(**5**) $[Cu_2L_2Cl_3]ClO_4$	703(127), 1 197 (35)
(**6**) $[Cu_2L_2Br_3]ClO_4$	489 (512), 707 (186), 1 210 (37)
(**7**) $[Cu_2L_2Br_2]Br_2{\cdot}2H_2O$	479 (sh) (784), 636 (720), 1 134 (117)
(**8**) $[Cu_2L_2(CH_3CO_2)_2][PF_6]_2$	642 (141), 1 090 (82)
(**9**) $[Cu_2L_2(C_2O_4)][ClO_4]_2$	635 (115), 1 097 (66)
(**14**) $[Cu_2L'_2(C_2O_4)][ClO_4]_2$	616 (110), 940 (29)
(**10**) $[Cu_2L_2(Cl_2C_6O_4)][ClO_4]_2$	608 (sh) (341), 1 170 (87)
(**11**) $[Cu_2L_2(H_2C_6O_4)][ClO_4]_2$	564 (557), 618 (507), 1 012 (285)
(**12**) $[Cu_2L_2\{(HN)_2C_2O_2\}][B(C_6H_5)_4]_2$	609 (153), 950 (52)
(**13**) $[Cu_2L_2(N_3)(OH)][ClO_4]_2$	661 (200), 1 038 (34)

* Solid-state spectra agree well with these spectra.

complex[6a] prepared *in situ* with azide ion in 1:1 ratio. Interestingly the azide ion bridges in an end-on fashion (see later).

Infrared Spectra.—The presence or absence of certain bands in the generally complicated i.r. spectra have been utilized to establish the nature of the complexes. Relevant bands are listed in Table 1. All of the perchlorate salts show strong bands near 1 100 (antisymmetric stretch) and sharp bands at 620—605 cm^{-1} (antisymmetric bend), indicative of unco-ordinated perchlorate anions.

It has been proprosed[11] that 'infrared criteria for bonding mode are reliable for thiocyanate complexes, although occasionally ambiguous.' The thiocyanate group can function as a unidentate ligand in two ways depending on whether the nitrogen or the sulphur atom is bonded to the metal. It also functions as a bridging ligand, M–NCS–M. The distinction of these possibilities is usually attempted by using i.r. spectroscopy[12] but of the three principal regions *viz.* ν(CN), ν(CS), and δ(NCS), the last two are difficult to assign because of absorptions due to L in these regions. The spectrum of complex (**1**) shows two well resolved bands of nearly equal intensity at 2 100 and 2 050 cm^{-1}, in the region expected for ν_{asym}(CN). Splitting of this order for the antisymmetric stretching vibration has previously been shown[12] to occur when two different kinds of NCS groups occur in the same molecule. The band at 2 100 cm^{-1} falls in the region expected for end-to-end bridging NCS and that at 2 050 cm^{-1} in the region expected for terminal NCS. Additionally, the lack of any absorption in the region 650—740 cm^{-1} argues strongly in favour of the absence of sulphur-bonded terminal NCS groups. The presence of a NCS stretching vibration at 2 100 cm^{-1} suggests that this group is co-ordinated to the copper atom in an end-to-end fashion.

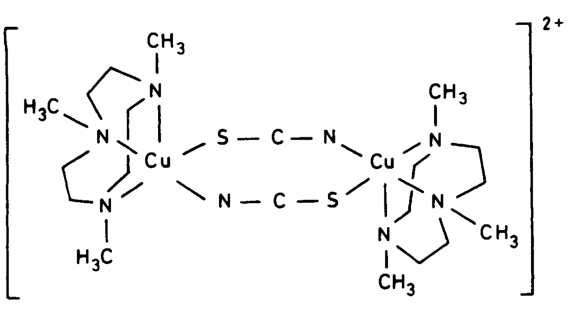
The position of the hydroxide stretch at 3 360 cm^{-1} for complex (**4**) and 3 400 cm^{-1} for (**7**) suggests the presence of H_2O molecules as water of hydration. The δ(H–O–H) vibrations at 1 610 cm^{-1} for (**4**) and 1 600 cm^{-1} for (**7**) are also observed. The acetato-complex (**8**), shows two ν(CO) bands at 1 581 and 1 429 cm^{-1}, which are very close to the two values of free acetate ion, showing the bridging character of the acetate groups.[13]

The i.r. spectra of complexes (**9**) and (**14**) exhibit only two ν(CO) bands, 1 630 and 1 355 cm^{-1} for (**9**) and 1 655 and 1 340 cm^{-1} for (**14**). This is a strong indication[13] that the oxalato anion is present as a bridging and quadridentate group, forming five-membered chelate rings with the copper atoms. Additionally, the bands at 730 cm^{-1} for (**9**) and 760 cm^{-1} for (**14**) are attributed to the deformation δ(OCO). Complex (**12**) shows bands at 3 300, 1 605, and 1 565 cm^{-1} attributable to the ν(NH) and ν(CO) stretching vibrations of the oxamidato ligand. Additionally three bands at 730, 720, and 700 cm^{-1} are observed for the tetraphenylborate stretch.

The free hydranilic and chloranilic acids have appreciable i.r. absorption in the region of 3 400 cm^{-1}. This absorption is missing in the spectra of copper complexes (**10**) and (**11**) indicating that the enolic hydrogen atoms are lost on chelation. The carbonyl stretching vibrations at 1 510 cm^{-1} for (**10**) and 1 520 cm^{-1} for (**11**) indicate a strong reduction of the C–O bond order upon complexation.

Complex (**13**) exhibits a sharp band of medium intensity at 3 540 cm^{-1} which is assigned to the bridging O–H stretch on the basis of previous observations,[6a] (bridging O–H stretching bands for waters of hydration are broad and occur at 3 400—3 300 cm^{-1}). I.r. bands due to azide ligation are observed for (**13**), a strong absorption, $\nu_{asym}(N_3)$, at 2 050 cm^{-1} and a weak peak at ≈1 300 cm^{-1} [$\nu_{sym}(N_3)$] which has not been identified unambiguously due to overlapping from bands due to the co-ordinated macrocycle. Complexes with terminal and μ-1,3-azido ligands also show similar absorptions.[6c] This point will be discussed later (see magnetic susceptibility measurements). These observations complement ours and those of other workers,[14] who have concluded that azide i.r. absorptions are not diagnostic of the mode of co-ordination.

Electronic Absorption Spectra.[15]—The electronic spectra of the complexes have been measured both in solution and in the solid state. The absorption maxima with the corresponding absorption coefficients in methanol and/or acetonitrile solutions are given in Table 2. The diffuse reflectance spectra measured as KBr disks agree well with the solution spectra, showing that no dissociation occurs in solution. Since the ligands do not show any bands in the visible region, the bands observed are definitely *d–d* bands of copper. The observation of medium-intensity band close to 16 000 cm^{-1} (625 nm) in the electronic spectrum of the complexes is consistent with tetragonal, square pyramidal, or octahedral geometry around the copper atom, indicating co-ordination of halogen, oxygen, or nitrogen atoms of the coligands in addition to the cyclic amine. As the data in Table 2 show, each complex exhibits at least two *d–d* bands in the visible region strongly indicating the



A

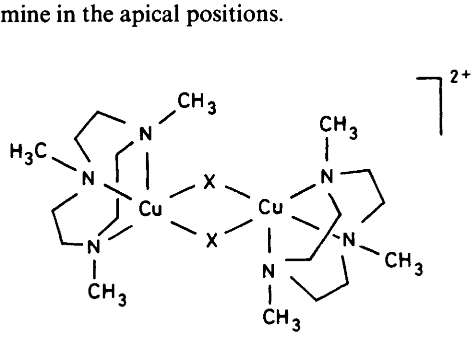
(1) SCN

(2) ClO$_4$

presence of five-co-ordinated copper(II) ions with a CuN_3X_2 core.

The electronic spectra of complexes (1) and (2) are very similar to those of $[Cu_2L_2(\mu\text{-}N_3)(N_3)_2]^+$ and $[Cu_2L_2(\mu\text{-}N_3)_2(ClO_4)_2]$ described previously.[6c] This is an indication of the fact that the copper(II) centres in (1) and (2) are also square-based pyramidal. Considering the analytical, i.r. and electronic spectral data we propose the structures shown. Additional support for this proposal emerges from the magnetic data, discussed later.

The energy-level diagrams for the copper(II) ions in ligand fields of square-based pyramidal (C_{4v}) and trigonal-bipyramidal (D_{3h}) symmetries predict three and two bands respectively. It has been shown by Hathaway [15] that it is possible to predict the stereochemistry of the local copper(II) ion environment in complexes of unknown crystal structures from the positions and intensities of the *d–d* transitions of CuX_5 chromophores. In general trigonal-bipyramidal complexes with $^2A'_1$ ground states exhibit a single, relatively intense band at 12 500 ± 1 500 cm^{-1}; on the other hand the electronic spectra of square-based pyramidal complexes consist of two clearly resolved bands covering the range 15 000 ± 2 000 cm^{-1}. Based on the above arguments, a square-pyramidal structure is assigned to all complexes listed in Table 2.Thus the geometries around the two copper(II) ions are pseudo-square-based pyramidal with each metal ion bonded to two nitrogen atoms of the macrocyclic ligand, two other donor atoms (chlorine, bromine, oxygen, or nitrogen) in the basal plane, and the third nitrogen atom of the cyclic amine in the apical positions.



E.S.R. Spectra.—The g values obtained from the X-band e.s.r. spectra of polycrystalline samples at 120 K are given in Table 3. The spectra of polycrystalline copper(II) complexes exhibiting two types of g values, $g_\parallel > g_\perp$, have been used [15] to distinguish unambiguously between $d_{x^2-y^2}$ and d_{z^2} ground states for which $g_\parallel > g_\perp$ and $g_\perp > g_\parallel \approx 2.00$, respectively. The copper complexes studied here show a pronounced peak ($g_\perp \approx 2.05$) and a broad shallow peak ($g_\parallel \approx 2.15$) typical of a d^9 complex possessing axial symmetry and with the unpaired electron present in the $d_{x^2-y^2}$ orbital. Except for complexes (1) and (2), no half-field transition, $\Delta M_s = 2$, is observed, which indicates a weak zero-field splitting.

In axial symmetry the g values are related by the expression $G = (g_\parallel - 2)/(g_\perp - 2)$, which measures the exchange interaction between copper centres in the polycrystalline solid; if $G > 4$ the exchange interaction is negligible, $G < 4$ indicates considerable exchange interation. The calculated G values are given in Table 3.

Magnetic Susceptibility.—Variable-temperature magnetic susceptibility data for the complexes were measured between 100 and 300 K with use of the Faraday method. Some representative plots of magnetic susceptibility *vs.* temperature are shown in the Figure. The magnetic parameters (Table 3) were estimated as g_{mag} and J from a least-squares fitting of the susceptibility data by the Bleaney–Bowers equation (1) for

$$\chi_M = \frac{N\beta g^2}{3kT}[1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1} \qquad (1)$$

simple copper(II) dimers, where $2J$ is the energy difference between the singlet and triplet states. The solid lines in the Figure represent these fits. The variations in g_{mag} values are not significant and result from the fitting method. Magnetic susceptibility data for all complexes, except (7) show unambiguously spin–spin interactions (binuclear nature of the complexes) occurring *via* a superexchange pathway rather than a direct metal–metal interaction. The Cu···Cu distance in our binuclear systems lies in the estimated range of ≈3.6—7.6 Å, based on the Cu···Cu distances of similar complexes for which structural data are available.[8,16] This separation generally rules out any significant amount of direct copper–copper interaction. The large effect of the nature of the bridging moiety on the paramagnetism of the complex substantiates this superexchange mechanism.

Complexes (1) and (2) show antiferromagnetic behaviour with singlet–triplet energy gap of 30 and 40 cm^{-1}, respectively, indicating their binuclear nature. The difference in J values may be due to the different anions. Spectroscopic data for (1) and (2) have already suggested the close to square-pyramidal stereochemistry of the d^9 copper(II) ions with $(d_{x^2-y^2})^1$ ground states. The major σ pathway for the interaction of these magnetic orbitals containing the unpaired electron involves thiocyanate ligands, which bridge these $d_{x^2-y^2}$ orbitals. In this connection, it is interesting to compare the isoelectronic azide, N_3^-, and the monoanion of cyanamide, $HNCN^-$, with thiocyanate as magnetic-exchange propagating bridges in analogous copper(II) complexes with 1,4,7-trimethyl-1,4,7-triazacyclononane. The observation that thiocyanate bridges provide less effective pathways for spin–spin interactions than the isoelectronic azide and $HNCN^-$ [6b,c,17] can be understood on the basis of the poor effective overlap between the magnetic orbitals, *i.e.* those holding the unpaired electron, involved in the binuclear unit, as observed for related compounds.[18] We would point out in this connection that the bis(μ-hydrogen cyanamido)–dicopper(II) complex has a distorted trigonal-bipyramidal[6b] geometry with a d_{z^2} ground state.

The χ_{Cu} (and μ_{Cu}) *versus* temperature behaviour of complexes (3)—(5) shows a slight increase in μ_{Cu} (Table 3) with decreasing temperature, compatible with weak overall ferromagnetic coupling. In other words, the J_{ferro} contribution to the overall J value is slightly larger than the $J_{antiferro}$ component. With the present susceptibility data it is notoriously difficult to estimate J with any degree of accuracy. The proper conclusion here is that these complexes exhibit weak ferromagnetic coupling with

Table 3. Magnetic susceptibility and e.s.r. parameters

Complex	$2J$/cm^{-1}	g_{mag}	$g_\perp$	$g_\parallel$	$\langle g \rangle$	G
(**1**) $[Cu_2L_2(\mu\text{-}SCN)_2][SCN]_2$	−30	2.00	2.07	2.11	2.08	1.68
(**2**) $[Cu_2L_2(\mu\text{-}SCN)_2][ClO_4]_2$	−40	2.00				
(**8**) $[Cu_2L_2(\mu\text{-}CH_2CO_2)_2][PF_6]_2$	−92	2.25	2.07	2.12	2.09	1.64
(**9**) $[Cu_2L_2(\mu\text{-}C_2O_4)][ClO_4]_2$	−300	2.10	2.10	2.15	2.11	1.15
(**14**) $[Cu_2L'_2(\mu\text{-}C_2O_4)][ClO_4]_2$	−60	2.10	2.08	2.18	2.11	2.25
(**12**) $[Cu_2L_2\{\mu\text{-}(HN)_2C_2O_2\}][B(C_6H_5)]_2$	−460	2.15				
(**10**) $[Cu_2L_2(\mu\text{-}Cl_2C_6O_4)][ClO_4]_2$	−60	2.40				
(**11**) $[Cu_2L_2(\mu\text{-}H_2C_6O_4)][ClO_4]_2$	−40	2.40	2.07	2.16	2.1	2.37
(**13**) $[Cu_2L_2(\mu\text{-}N_3)(\mu\text{-}OH)][ClO_4]_2$	+44	2.15				
	μ_B per Cu (T/K)		θ/K			
(**3**) $[Cu_2L_2(\mu\text{-}Cl)_2][ClO_4]_2$	2.08 (103) 1.89 (293)		+24		2.10	Quasi-isotropic
(**4**) $[Cu_2L_2(\mu\text{-}Cl)_2]Cl_2\cdot 2H_2O$	2.07 (103) 1.94 (293)		+12.1			
(**5**) $[Cu_2L_2(\mu\text{-}Cl)Cl_2]ClO_4$	2.03 (103) 1.95 (293)		+7.4		2.10	Quasi-isotropic
(**6**) $[Cu_2L_2(\mu\text{-}Br)Br_2]ClO_4$	2.01 (103) 2.16 (293)		−18		2.08	Quasi-isotropic
(**7**) $[Cu_2L_2(\mu\text{-}Br)_2]Br_2\cdot 2H_2O$	1.7					

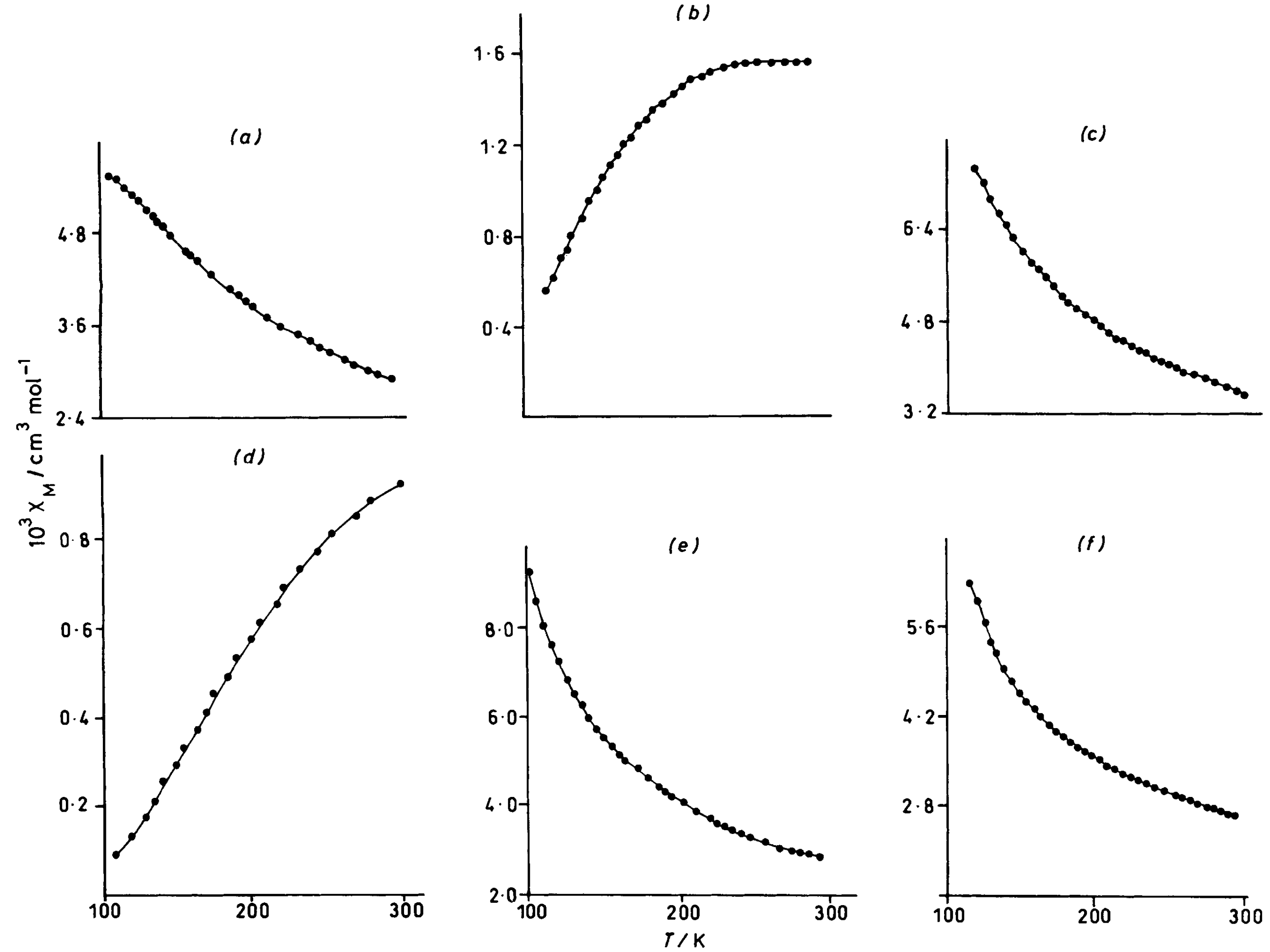
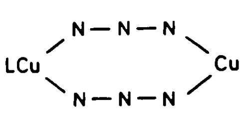


Figure. Plots of magnetic susceptibility *vs.* temperature for complexes (**8**) (*a*), (**9**) (*b*), (**10**), (*c*), (**12**) (*d*), (**13**) (*e*), and (**14**) (*f*). The solid lines represent the best least-squares fit of the experimental susceptibility data to the theoretical equation (see text)

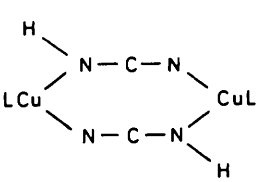
triplet ground states. Similar μ-chloro bridged copper(II) dimers exhibiting ferromagnetic interactions are known.[16a]

In contrast to the chloro-bridged complexes, μ-bromo complex (**6**) shows antiferromagnetic behaviour with a J value of -20 cm^{-1}. That the magnetic exchange behaviour changes from ferromagnetic to antiferromagnetic on changing the bridging anion from chloride to bromide or the reverse is well documented.[16b,19] The magnetic data for (**7**) adhere closely to



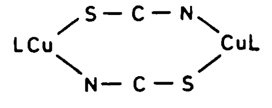
$2J < -800$ cm^{-1}

(ref. 6c)



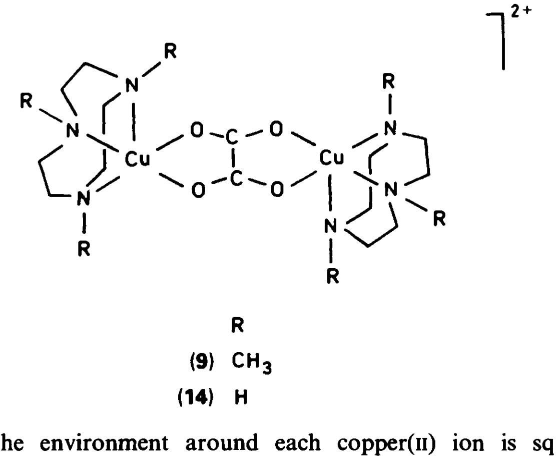
$2J = -380$ cm^{-1}

refs. 6b, 17



$2J = -40$ cm^{-1}

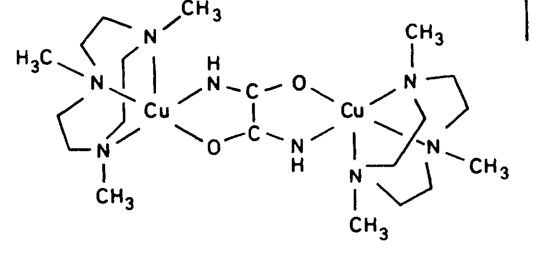
the Curie law with a temperature-independent magnetic moment of 1.71 μ_B per Cu. Although we have formulated **(7)** as a binuclear complex with a di-μ-bromo bridge and two non-co-ordinating bromide anions, in analogy to **(4)** (Table 2), it could equally well be a mononuclear copper(II) complex. The magnetic properties of **(9)** and **(14)** are given in the Figure. The susceptibility of **(9)** decreases strongly with decreasing temperature. A plateau is reached at 250—300 K. The magnetic moment per Cu ion varies from 1.34 μ_B at 293 K to 0.48 μ_B at 103 K. Least-squares fitting of the susceptibility data by the Bleaney–Bowers equation (1) lead to parameters given in Table 3. For complex **(9)** the antiferromagnetic interaction is strong with $2J = -300$ cm^{-1} and for **(14)** it is much weaker with $2J = -60$ cm^{-1}. Thus the following binuclear structure for **(9)** and **(14)** is in complete agreement with the presently available data for these complexes.



	R
(9)	CH_3
(14)	H

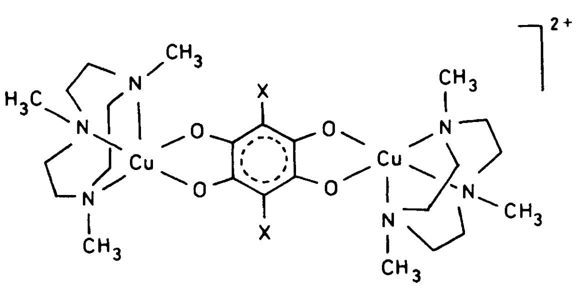
The environment around each copper(II) ion is square pyramidal with two nitrogen atoms of the amine and two oxygen atoms of the oxalate in the basal plane, CuN_2O_2, the third nitrogen atom of the amine occupying the apical position. This proposal is further supported by the observations that these cyclic amines co-ordinate facially as evidenced by various crystal-structure determinations.[5] The strong antiferromagnetic interaction in **(9)** can be interpreted by considering the delocalization of each magnetic orbital of Cu^{II}, $d_{x^2-y^2}$, in the same plane as the oxalato ligand. This picture fits very well with Kahn's model for designing μ-oxalato-dicopper(II) complexes exhibiting expected magnetic properties.[16f] The much weaker interaction in **(14)** can be understood by envisaging that the geometry around each copper(II) has deviated from a square pyramid toward a trigonal bipyramid, but is still far from purely trigonal bipyramidal as evidenced by the e.s.r. spectrum (Table 3). With increasing trigonal character of the CuN_3O_2 chromophore the d_{z^2} character of the magnetic orbital increases and hence a reduction in the magnetic exchange interaction is observed.

For complex **(12)** the antiferromagnetic interaction is even stronger than that in **(9)** with a singlet–triplet energy gap of 460 cm^{-1} as would be expected. The observation[20] that a μ-oxamidato bridge is more efficient than a μ-oxalato bridge in propagating antiferromagnetic exchange interactions has been attributed by Kahn and co-workers[3b,16g,21] to the lower electronegativity of nitrogen as compared to oxygen. Thus based on all data at hand we propose the following structure with an oxamidato bridge in the *trans* configuration for the cationic part of **(12)**. The *X*-ray structure of $[Cu_2(pedien)_2\{\mu\text{-}(HN)_2C_2O_2\}][PF_6]_2$ (pedien = *NNN'N''N''*-pentaethyldiethylenetriamine)[16h] lends further support to this proposal.



The magnetic moment of the di-μ-actetato complex **(8)** varies from 1.61 μ_B at 293 K to 1.33 μ_B per Cu at 103 K indicating a medium-strength intramolecular antiferromagnetic coupling with a singlet–triplet splitting of 92 cm^{-1}. Recently Murray and co-workers[16d] observed a $2J$ value of -72 cm^{-1} for a di-μ-acetato complex of this type but with a μ-phenolate bridge. The low overall J value of complex **(8)** in comparison to the μ-oxalato complex **(9)** may be due to the fact that the acetate groups connect basal plane ($d_{x^2-y^2}$) positions on one Cu with apical (d_{z^2}) positions on the other, thus leading to a greater J_{ferro} contribution from these pathways. Thus a larger d_{z^2} contribution to the copper(II) state is expected in the di-μ-acetato case than in complex **(9)**, decreasing the $d_{x^2-y^2}$ character and hence also the antiferromagnetic exchange interaction. On the basis of the spin-exchange coupling constants J (Table 3), the extent of trigonal distortion of the CuN_3O_2 unit from square pyramidal decreases in the order **(14)** > **(8)** ≫ **(9)**. It is implicitly assumed in this analysis that the displacement of the Cu atom from the basal plane is the same in these complexes.

The chloroanilate bridge has been claimed[16i] to bear a qualitative resemblance to bridged oxalate complexes, but the intramolecular Cu $\cdots$ Cu separation changes from ≈5.2 Å for μ-oxalate complexes to ≈7.9 Å for μ-chloroanilate complexes. In the copper(II) binuclear compounds containing derivatives of the 2,5-dihydroxy-1,4-benzoquinone dianion as bridging ligands, **(10)** and **(11)**, the Cu $\cdots$ Cu separation is expected to be around 7.9 Å, as evidenced by structural data available for similar compounds.[8,16i] In full accord with expectation, medium–weak antiferromagnetic interaction is observed for **(10)** ($2J = -60$ cm^{-1}) and **(11)** ($2J = -40$ cm^{-1}). Thus the following structure is envisaged for these complexes. Each copper ion is located in distorted square-pyramidal surroundings with two nitrogen atoms of the cyclic amine and two oxygen atoms of the 2,5-dihydroxy-1,4-benzoquinone dianion in the basal plane and the third nitrogen atom of the 1,4,7-trimethyl-1,4,7-triazacyclononane in the apical position. E.s.r. data are in accordance with this proposal. A similar structure has been described by Kahn and co-workers[8] for a μ-iodanilato



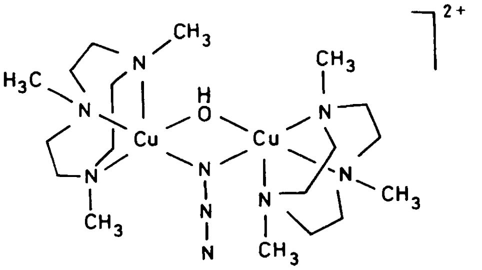
X

(10) Cl

(11) H

compound containing *NNN'N'*-tetramethylenediamine (tmen) as the terminal ligands. For a series of compounds of formula $[Cu_2(tmen)_2A][ClO_4]_2$ where A^{2-} is a derivative of the dianion of 2,5-dihydroxy-1,4-benzoquinone with X groups (H, Cl, Br, I, or NO_2) in the 3,6 positions, these workers have also observed an intramolecular antiferromagnetic interaction with a singlet–triplet energy gap in the range of 17—26 cm^{-1}. It should be noted here that antiferromagnetic interactions in our compounds **(10)** and **(11)** seem to be much stronger than in the above-mentioned compounds. In contrast, in the μ-chloranilato complex described by Pierpont *et al*[16i] with pentamethyldiethylenetriamine as the terminal ligands no spin coupling was detected, although the copper surroundings are close to square pyramidal as in **(10)** and **(11)**, but the basal planes containing the CuN_2O_2 chromophores are perpendicular to the plane of the bridging network.

The μ-hydroxo-μ-azido complex **(13)** shows a slight increase in μ_{Cu} with decreasing temperature, compatible with weak ferromagnetic coupling ($J \approx +22$ cm^{-1}). As has already been pointed out, little significance should be attached to the absolute value of J. Kahn[22] in an elegant analysis showed that the stabilization of the triplet ground state is characteristic of the presence of an end-on azido bridge in binuclear copper(II) complexes. Hence, on the basis of analytical, spectroscopic, and magnetic data, we propose the following structure for the compound **(13)**.* A similar compound with tmen as the terminal ligand has been structurally characterized.[23]



In summary, we have demonstrated that the macrocyclic N_3-donor ligand 1,4,7-trimethyl-1,4,7-triazacyclononane possesses the versatile ability of forming stable binuclear copper(II) complexes with distorted square-based pyramidal environments and containing multiple-atom bridging ligands. The estimated Cu ··· Cu separation lies in the range of 3.6—7.6 Å and can be extended to 11.25 Å[6d] for binuclear copper(II) complexes exhibiting intramolecular antiferromagnetic interactions with this tridentate N-donor ligand.

Acknowledgements

We thank Professor K. Wieghardt for his continuous help and interest. The receipt of a grant from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Our thanks are also due to Dr. D. March (Göttingen) and Dr. W. Oettmeier (Bochum) for the e.s.r. measurements.

References

1 See, for example, 'Biological and Inorganic Copper Chemistry,' eds. K. D. Karlin and J. Zubieta, Adenine, Guilderland, New York, 1986.

2 E. I. Solomon in 'Copper Proteins,' ed. T. G. Spiro, Wiley-Interscience, New York, 1981; J. A. Fee, *Struct. Bonding (Berlin)*, 1975, **23**, 1.

3 (*a*) 'Magneto-Structural Correlations in Exchange Coupled Systems,' eds. R. D. Willett, D. Gatteschi, and O. Kahn, NATO ASI Ser. No. 140, Reidel, Dordrecht, 1985; (*b*) O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.

4 D. N. Hendrickson, in 'Magneto-Structural Correlations in Exchange Coupled Systems,' eds. R. D. Willett, D. Gatteschi, and O. Kahn, NATO ASI Ser. No. 140, Reidel, Dordrecht, 1985, pp. 523—554.

5 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 330; P. Chaudhuri, H-J. Küppers, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1988, 1367; P. Chaudhuri, M. Winter, H-J. Küppers, K. Weighardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1987, **26**, 3302; P. Chaudhuri and K. Oder, *J. Organomet. Chem.*, 1989, **367**, 249.

6 (*a*) P. Chaudhuri, D. Ventur, K. Wieghardt, E. M. Peters, K. Peters, and A. Simon, *Angew. Chem.*, 1985, **97**, 55; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 57; (*b*) P. Chaudhuri, K. Wieghardt, B. Nuber, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1985, 265; (*c*) P. Chaudhuri, K. Oder, K. Weighardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 2818; (*d*) P. Chaudhuri, K. Oder, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, and J. Weiss, *J. Am. Chem. Soc.*, 1988, **110**, 3657.

7 R. D. Willett, in 'Magneto-Structural Correlations in Exchange Coupled Systems,' eds. R. D. Willett, D. Gatteschi, and O. Kahn, Reidel, Dordrecht, 1985, pp. 3489—420; W. Hatfield, *ibid.*, pp. 555—602.

8 F. Tinti, M. Verdaguer, O. Kahn, and J. M. Savariault, *Inorg. Chem.*, 1987, **26**, 2380 and refs. therein.

9 K. Wieghardt, P. Chaudhuri, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1982, **21**, 3086.

10 L. Goswami, S. Sarker, and D. Banerjea, *Z. Anorg. Allg. Chem.*, 1977, **435**, 301; A. K. Basak and C. Chatterjee, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 318.

11 R. A. Bailey, S. L. Kozack, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.*, 1971, **6**, 402; M. G. B. Drew, B. P. Murphy, J. Nelson, and S. W. Nelson, *J. Chem. Soc., Dalton Trans.*, 1987, 873.

12 J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590; A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665; R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, 1966, **22**, 1081; J. Chatt and L. A. Duncanson, *Nature (London)*, 1956, **178**, 997; A. H. Norbury, *Adv. Inorg. Chem., Radiochem.*, 1975, **17**, 232.

13 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley, New York, 1978.

14 K. D. Karlin, J. C. Hayes, J. P. Hutchinson, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1983, 376; Z. Dori and R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247; M. G. B. Drew, J. Nelson, F. Esho, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1982, 1837.

15 A. P. B. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1985; B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55; B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143 and refs. therein; B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1970, **5**, 1 and refs. therein.

16 (*a*) S. K. Hoffmann, D. K. Towle, W. E. Hatfield, P. Chaudhuri, and K. Wieghardt, *Inorg. Chem.*, 1985, **24**, 1307 and refs. therein; (*b*) D. K. Towle, S. K. Hoffmann, W. E. Hatfield, P. Singh, P. Chaudhuri, and K. Wieghardt, *ibid.*, p. 4393 and refs. therein; (*c*) M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 1974, 556; (*d*) K. Bertoncello, G. D. Fallon, J. H. Hodgkin, and K. S. Murray, *Inorg. Chem.*, 1988, **27**, 4750; (*e*) N. F. Curtis, I. R. N. McCormick, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1537; (*f*) M.

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* *Note added at proof.* The proposed structure of compound **(13)** has been confirmed by *X*-ray crystallography.

Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalle, and O. Kahn, *Inorg. Chem.*, 1984, **23**, 3808 and refs. therein; (*g*) M. Verdaguer, O. Kahn, M. Julve, and A. Gleizes, *Nouv. J. Chim.*, 1985, **9**, 325; (*h*) J. Sletten, *Acta Chem. Scand., Ser. A*, 1985, **39**, 475; (*i*) C. G. Pierpont, L. C. Francesconi, and D. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367.

17 P. Chaudhuri and W. E. Hatfield, unpublished work.

18 G. R. Hall, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 1956; J. G. Haasnoot, W. L. Driessen, and J. Reedijk, *ibid.*, 1984, **23**, 2803; J. L. Mesa, T. Rojo, M. I. Arriortua, G. Villeneuve, J. V. Folgado, A. Beltrán-Porter, and D. Beltrán-Porter, *J. Chem. Soc., Dalton Trans.*, 1989, 53.

19 M. Mégnamisi-Bélombé and M. A. Novotny, *Inorg. Chem.*, 1980, **19**, 2470.

20 K. Nonoyama, H. Ojima, K. Ohki, and M. Nonoyama, *Inorg. Chim. Acta*, 1980, **41**, 155.

21 Y. Journaux, J. Sletten, and O. Kahn, *Inorg. Chem.*, 1985, **24**, 4063.

22 O. Kahn, *Comments Inorg. Chem.*, 1984, **3**, 105.

23 O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, and Y. Jeannin, *Inorg. Chem.*, 1983, **22**, 2877.

Received 3rd *November* 1989; *Paper* 9/04886C