Dinuclear Metal Complexes. Part 3.† Preparation and Properties of Hydroxo-bridged Dicopper(II) Complexes ‡

Sanat Kumar Mandal and Kamalaksha Nag *
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Hydroxo-bridged dicopper(II) complexes of five-co-ordinate acyclic diazadiamine NNNNO-bonded ligands have been synthesised. These compounds are obtained in high yield by reacting the sodium salt of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde, copper perchlorate, and the diamines 1,3-diaminopropane, 1,2-diaminoethane, and 1,2-diaminopropane, respectively in aqueous medium under high dilution. Similar reactions with 1,3-diacetyl- or 1,3-dibenzoyl-2-hydroxy-5-methylbenzene in water–methanol afford similar acyclic complexes in lower yield along with their corresponding NNNNOO-bonded macrocyclic complexes. The hydroxy bridging group in the acyclic complexes can be replaced by other bridges like methoxide, *p*-nitrophenolate, pyrazolyl, and by reaction with 2-hydroxy-5-methylacetophenone. Variously 6,12-substituted dicopper(II) complexes of the macrocycle 7,11; 19,23-dimetheno-9,21-dimethyl[1,5,13,17]tetra-azacyclotetracosa-5,7,9,12,17,19,21,24-octaene-25,26-diol (H_2L^5) can be obtained by reacting the above unsubstituted acyclic complex with 1,3-diacetyl- or 1,3-dibenzoyl-2-hydroxy-5-methylbenzene. The acyclic tetra-amine hydroxo-bridged dicopper(II) complex shows similar reactivity to the diazadiamine derivative and the corresponding macrocyclic complexes containing both aza and amine linkages have been synthesised. All these compounds have been characterised from their magnetic moments, i.r., and electronic spectra. The electrochemical studies of the acyclic diazadiamine and tetra-amine hydroxo-bridged dicopper(II) complexes have revealed irreversible reductions followed by decomposition of the reduced species. One of the diazadiamino macrocyclic complexes was found to undergo quasi-reversible one-electron reductions at two different potentials. The mechanism of formation of the unsubstituted macrocyclic complex $[Cu_2L^5][ClO_4]_2\cdot 2H_2O$ by reacting the corresponding hydroxo-bridged acyclic complex with 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde has been investigated.

Dinuclear copper complexes have received considerable attention from the standpoint of correlating spin–spin interactions between the two copper(II) centres and the structural framework in which they are contained.[1-4] During recent years there has been growing interest in designing dicopper complexes that would mimic the 'type 3' active site of copper proteins.[4-7] Model studies[8-14] have dealt with ligand environment, redox properties, magnetic interactions, and oxygen uptake of these active sites. Since the introduction of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde as the building block for dinucleating macrocyclic and non-macrocyclic ligands, extensive studies have been made on their metal complexes.[15-25] In two previous publications we have reported[26,27] the spectroscopic, magnetic, and redox properties of the dicopper(II) complexes of 1,3-diacyl/benzoyl-2-hydroxy-5-methylbenzene, (1) (R = R′ = H, Me, Pr^n, Ph; R = Me, R′ = Ph) and of the macrocycle 7,11; 19,23-dimetheno-9,21-dimethyl-[1,5,13,17]tetra-azacyclotetracosa-5,7,9,12,17,19,21,24-octaene-25,26-diol and some of its 6,12,18,24-substituted (Me_4; Pr^n_4; Ph_4; Ph, Me, Ph, Me) derivatives, (2). During the course of these studies we have discovered that the reaction between the sodium salts of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehydes or 1,3-diacetyl- and 1,3-dibenzoyl-derivatives with ω,ω′-diaminoalkanes in the presence of copper(II) perchlorate in dilute aqueous or aqueous methanol solution afford the hydroxo-bridged dicopper(II) complexes of the acyclic Schiff bases, (3). Here we report the reactivities and synthetic utilities of these complexes.

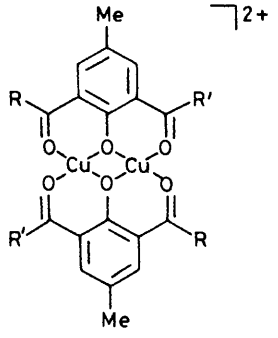
Experimental

Materials.—All chemicals were reagent grade and were used as received. 2-Hydroxy-5-methylbenzene-1,3-dicarbaldehyde (hmbdc), 1,3-diacetyl-2-hydroxy-5-methylbenzene (dahmb), 1,3-dibenzoyl-2-hydroxy-5-methylbenzene (dbhmb), and 3-benzoyl-2-hydroxy-5-methylacetophenone (bhmap) were prepared as described earlier.[27]

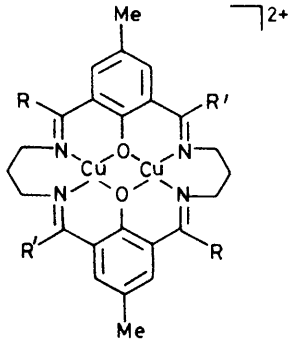
Preparation of the Complexes.—$[Cu_2L^1(OH)][ClO_4]_2\cdot nH_2O$ (3a)—(3c). The complex (3a) was prepared as follows. A mixture of hmbdc (1.64 g, 10 mmol), NaOH (0.4 g, 10 mmol), and water (5 cm^3) was ground to a paste in a mortar. This was added with stirring to boiling water (1 dm^3) when a clear yellow solution was obtained. A second solution of $Cu(ClO_4)_2\cdot 6H_2O$ (9.3 g, 25 mmol) and 1,3-diaminopropane (2.2 g, 30 mmol) in water (50 cm^3) was added to the first solution and boiled. The resulting deep blue solution was allowed to concentrate on a hot plate. When the volume of the solution reduced to *ca.* 100 cm^3, it was filtered hot. The filtrate was allowed to cool at ambient temperature and the blue crystalline product collected by filtration. The filtrate was further concentrated to *ca.* 30 cm^3, and on ice-cooling, a further crop of product was obtained. The combined material was recrystallised from boiling water, and dried over $CaCl_2$; yield 5 g (80%, based on hmbdc).

To a solution of dahmb (0.63 g, 2 mmol) and NaOH (0.08 g, 2 mmol) in methanol (150 cm^3) was added an aqueous solution (300 cm^3) of $Cu(ClO_4)_2\cdot 6H_2O$ (1.86 g, 5 mmol) and 1,3-diaminopropane (0.44 g, 6 mmol). The mixture was heated under reflux for 4 h, then filtered. The residue was primarily a mixture of $Cu(OH)_2$ and the macrocyclic complex (10b). The filtrate was reduced to *ca.* 25 cm^3 in a rotary evaporator, and allowed to crystallise at ambient temperature. After 2 d the blue crystals were collected by filtration. The product (3b) was purified by recrystallisation from hot water in which the possible contaminant (10b) is practically insoluble. It was dried over $CaCl_2$: yield 0.58 g (40% based on dahmb).

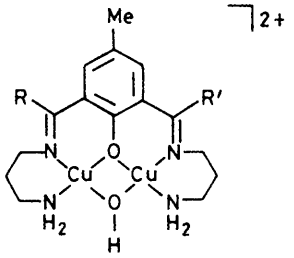
† Part 2 is ref. 27.
‡ *Non-S.I. unit employed*: B.M. = 9.274 × 10^{-24} J T^{-1}.



(1)



(2)



(3)

Starting from dbhmb, (3c) was obtained (40% yield) in the same way as (3b).

$[Cu_2L^2(OH)][ClO_4]_2 \cdot H_2O$ (4). This was obtained (80% yield) in essentially the same way as (3a) using 1,2-diaminoethane.

$[Cu_2L^3(OH)][ClO_4]_2 \cdot H_2O$ (5). This was also obtained as for (3a) using 1,2-diaminopropane (80% yield).

$[Cu_2L^1(OMe)][ClO_4]_2$ (6). Sodium metal (0.046 g, 2 mmol) was dissolved in dry methanol (30 cm^3) and (3a) (1.27 g, 2 mmol) added to it. The solution was refluxed for 0.5 h, filtered, and the volume of the filtrate reduced to 10 cm^3. This was kept in a stoppered flask in ice for 2 h; the crystals deposited were collected by filtration and recrystallised from dry methanol.

$[Cu_2L^1(OC_6H_4NO_2\text{-}p)][ClO_4]_2$ (7). To a methanol solution (50 cm^3) of (3a) (0.64 g, 1 mmol) was added *p*-nitrophenol (0.14 g, 1 mmol). The solution was refluxed for 3 h, cooled to room temperature, and filtered. The filtrate was allowed to evaporate slowly. After 1 d the crystals were collected by filtration and recrystallised from methanol.

$[Cu_2L^1(pz)][ClO_4]_2 \cdot H_2O$ (8). A mixture of (3a) (0.64 g, 1 mmol) and pyrazole (Hpz) (0.07 g, 1 mmol) in methanol (50 cm^3) was refluxed for 8 h. The solution was evaporated slowly at room temperature, the crystals collected after 1 d, and recrystallised from methanol.

$[Cu_2L^4][ClO_4]_2 \cdot H_2O$ (9). A methanol solution (50 cm^3) of (3a) (0.64 g, 1 mmol) and 2-hydroxy-5-methylacetophenone (0.15 g, 1 mmol) was refluxed for 20 h. The solution was concentrated to 20 cm^3, then cooled in ice for 2 h. The crystalline product was collected by filtration and recrystallised from methanol.

$[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$ (10a)—(10d). These compounds were obtained by the general procedure described below. A mixture (1 : 1 mol ratio) of (3a) and hmbdc [for (10a)], dahmb [for (10b)], dbhmb [for (10c)], or bhmap [for (10d)] in methanol (50 cm^3 for 2 mmol of reactants) was refluxed for 20 h, during which the product separated out. The compounds (10b)—(10d) were recrystallised from methanol; for (10a), product formation took place within 2 h and it was recrystallised from water.

NaL^6 (11). This compound was prepared essentially as reported in the literature [28] for the 1,2-diaminoethane derivative.

$[Cu_2L^6(OH)][ClO_4]_2 \cdot H_2O$ (12). An aqueous solution (20 cm^3) of NaL^6 (0.6 g, 2 mmol) and NaOH (0.1 g, 2.5 mmol) was slowly added with stirring to an aqueous solution (20 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.48 g, 4 mmol). The mixture was stirred for 15 min and then filtered. The filtrate was reduced to half volume and allowed to stand at room temperature for 12 h. The deep blue crystals were collected by filtration, recrystallised from water, and dried over $CaCl_2$; yield 1 g (80%).

Compounds (13) and (14) were prepared from (12) in the same way as described for (6) and (8) respectively.

$[Cu_2L^7][ClO_4]_2 \cdot 2H_2O$ (15a)—(15c). A (1 : 1) mixture of (12) (0.64 g, 1 mmol) and hmbdc [for (15a)], dahmb [for (15b)], or bhmap [for (15c)] in methanol (50 cm^3) was refluxed for 18 h. The solution was concentrated to *ca.* 20 cm^3, and on standing for a few hours the product crystallised out. Recrystallisation was effected from water, (15a), or methanol, (15b) and (15c).

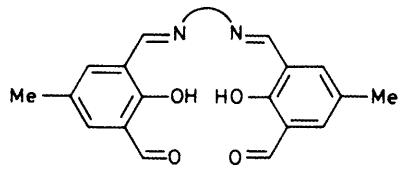
Analytical data for the complexes are given in Table 1.

Physical Measurements.—The equipment used was as described previously.[26,27]

Kinetic Studies.—The kinetics of formation of (10a) by reacting (3a) with hmbdc were investigated spectrophotometrically at 25 ± 0.2 °C. The concentration of (3a) was 2×10^{-3} mol dm^{-3} in acetonitrile and that of hmbdc was varied in the range 2×10^{-2} to 10^{-1} mol dm^{-3}. The change in absorbance was monitored at 630 nm. Reaction rates were followed for at least three half-lives. The pseudo-first-order rate constants were obtained by plotting $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ *vs.* t where A_0 and A_∞ are the initial and final absorbances of the complex species and A_t is that at time t.

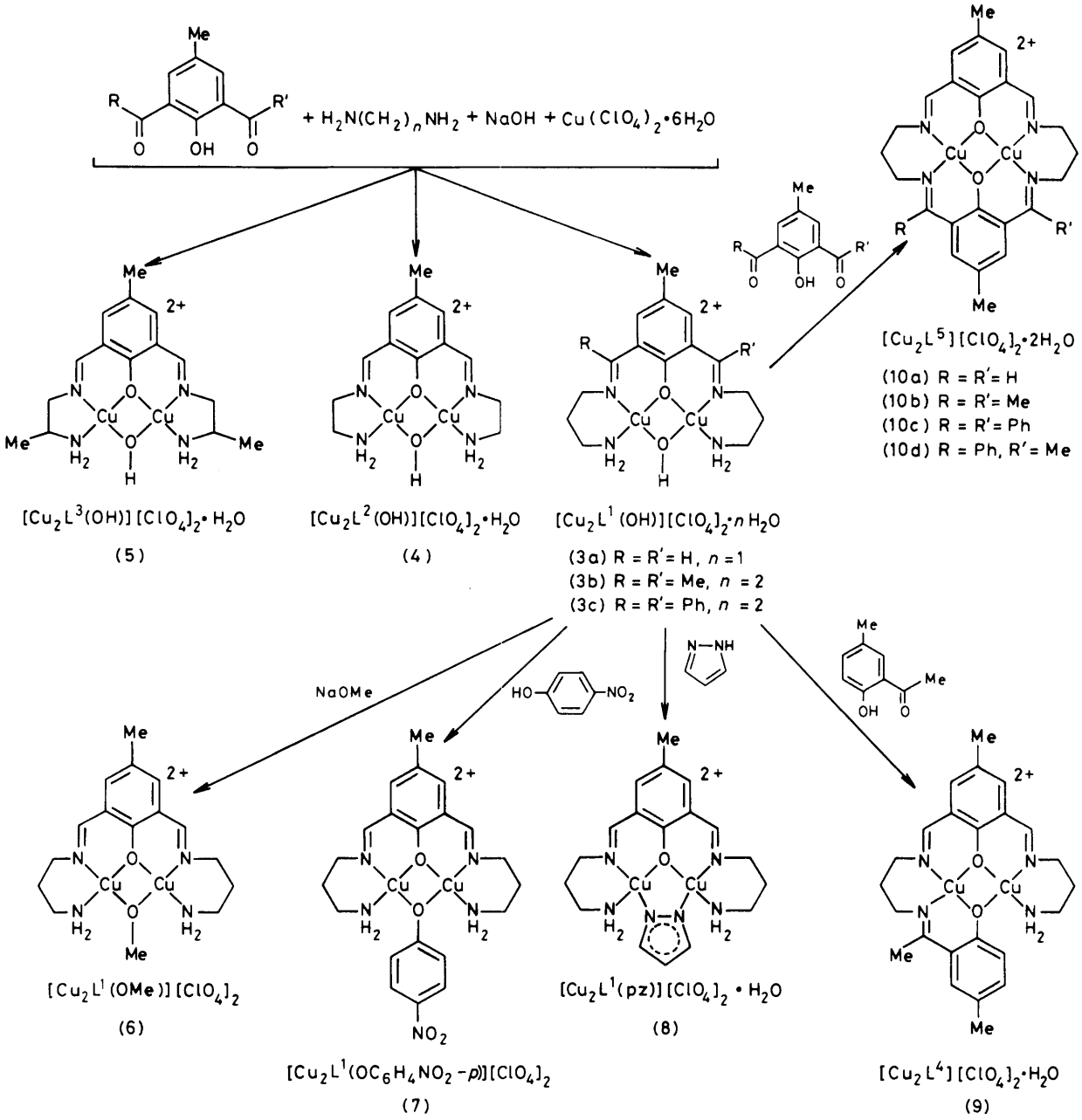
Results and Discussion

Synthesis of the Complexes.—In a previous publication we showed [27] that the macrocyclic dicopper(II) complexes (2) can be obtained either by reacting (1) with 1,3-diaminopropane or through a reaction involving 1,3-diacetyl- or 1,3-dibenzoyl-2-hydroxy-5-methylbenzene, copper(II) perchlorate,[26] and 1,3-diaminopropane in methanol or ethanol.[26] We now find that when the sodium salt of hmbdc is reacted with copper(II) perchlorate and ω,ω′-diaminoalkanes in aqueous solution under high dilution, instead of the expected macrocyclic complexes, the acyclic hydroxy-bridged dicopper(II) complexes (3a), (4), and (5) are obtained in almost quantitative yield. The reaction is quite remarkable in that only one end of the diamines has condensed with each part of the carbaldehyde moiety. This reaction differs from the other known condensation pattern of hmbdc with diaminoalkanes, resulting in the formation of *NN′*-alkylenebis(5-methyl-3-formylsalicylaldimine), (16).[16] Extension of the above reaction with



(16)

dahmb or dbhmb was difficult because the sodium salts are not soluble in water. Therefore a methanol–water mixture has to be used. Under these conditions the desired products (3b) and (3c) are obtained in reduced yield (40%) along with the corresponding macrocyclic complexes. The hydroxo-bridged compounds (3b) and (3c) were separated from their



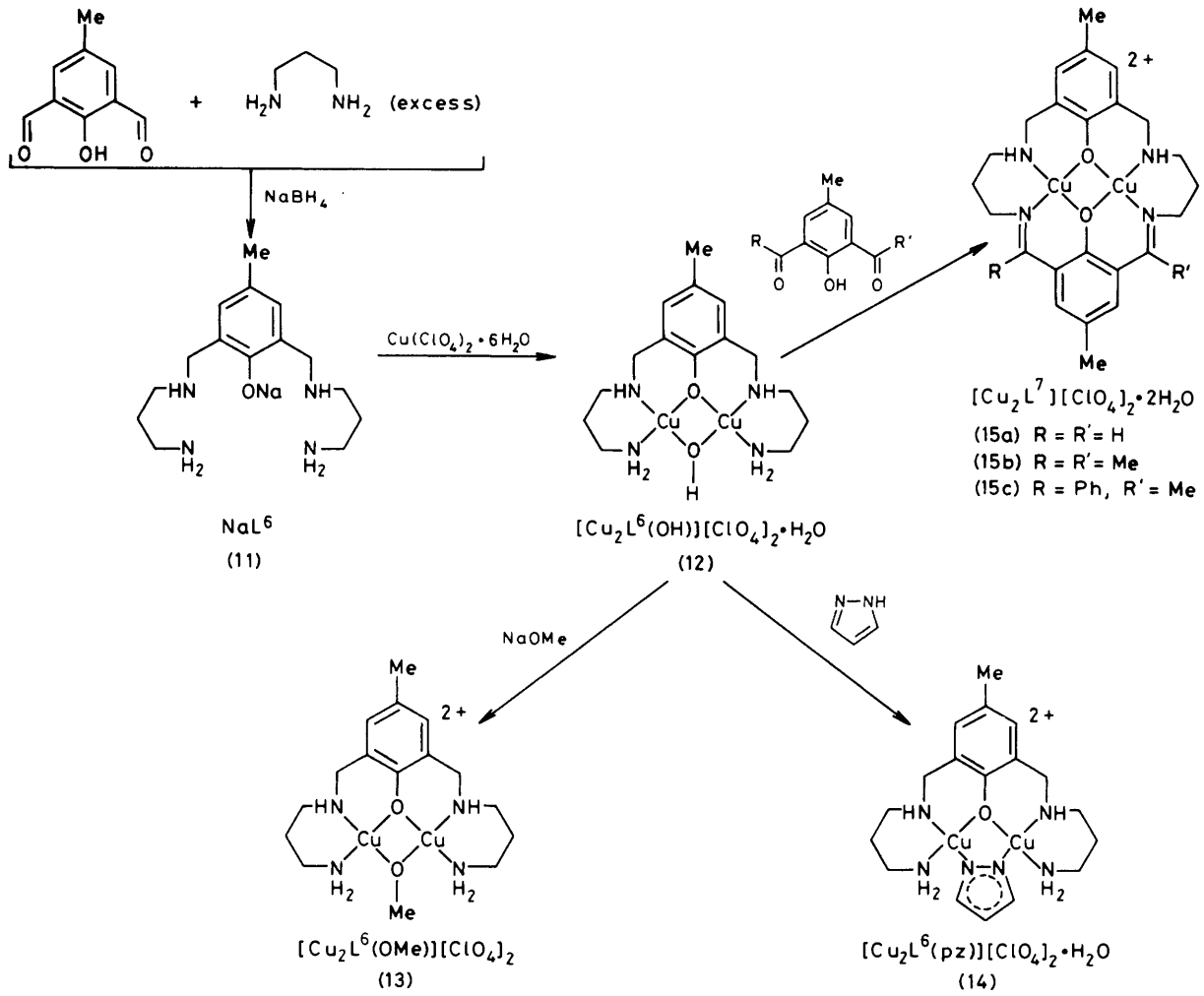
Scheme 1.

macrocyclic counterparts by using their differing solubilities.

The formation of the hydroxo-bridged complexes and their reactivities with various reagents are outlined in Scheme 1. The hydroxy group can be replaced by a methoxy bridge, *e.g.* (6) is obtained by reacting (3a) with NaOMe. The hydroxy group also reacts with weak organic acids and is eliminated as a water molecule; the anions of the deprotonated acids serve as the bridging ligand. In this way (7) and (8) have been obtained. Complex (9) provides an example where the hydroxy group is replaced by a phenoxo bridge and one free amino group is condensed with the phenolic ketone. The ease with which the products of these reactions are obtained demonstrates that a host of related other compounds can be synthesised. Of particular interest is the formation of the macrocyclic complexes (10) by reaction of (3a) with appropriate 1,3-diketophenols. It should be noted that by using this reaction it is possible to generate variously substituted macrocyclic complexes which otherwise are not accessible. The formation of (10a) is relatively fast (see kinetic studies) with respect to the other derivatives, apparently a consequence of steric effects.

Complex (12) has been synthesised following a suggested route reported in ref. 28. The reactions of (12) (Scheme 2) are quite similar to those of (3a). The macrocyclic compounds (15) are particularly interesting because in these compounds the two halves of the ring contain diamino and diaza moieties.

Infrared Spectra.—Pertinent i.r. data of the complexes are set out in Table 2. All the hydroxo-bridged complexes show a strong band at *ca.* 3 540 cm^{-1}, which can be distinguished[28,29] from the broad absorption centred at *ca.* 3 450 cm^{-1} due to the solvent water molecules in these and other compounds. Several bands arising in the region 3 350—3 100 cm^{-1} are due to symmetric and asymmetric N–H stretchings. For the tetraaza macrocyclic compounds (10a)—(10d) these bands are



Scheme 2.

Table 1. Analytical data for the dinuclear copper(II) complexes

Complex [a]	Colour	Analysis [b] (%) C	H	N	Cu
(3a) $[Cu_2L^1(OH)][ClO_4]_2 \cdot H_2O$	Blue	28.5 (28.3)	3.9 (4.1)	8.55 (8.8)	20.2 (20.0)
(3b) $[Cu_2L^1(OH)][ClO_4]_2 \cdot 2H_2O$	Blue	29.7 (29.9)	4.15 (4.7)	7.8 (8.2)	18.8 (18.65)
(3c) $[Cu_2L^1(OH)][ClO_4]_2 \cdot 2H_2O$	Green	39.95 (40.2)	4.25 (4.45)	7.0 (6.95)	15.65 (15.75)
(4) $[Cu_2L^2(OH)][ClO_4]_2 \cdot H_2O$	Blue	25.5 (25.65)	3.45 (3.6)	9.0 (9.2)	20.7 (20.9)
(5) $[Cu_2L^3(OH)][ClO_4]_2 \cdot H_2O$	Green	28.45 (28.3)	3.9 (4.1)	8.55 (8.8)	20.25 (19.95)
(6) $[Cu_2L^1(OMe)][ClO_4]_2$	Green	30.1 (30.45)	4.4 (4.1)	8.6 (8.85)	19.9 (20.1)
(7) $[Cu_2L^1(OC_6H_4NO_2\text{-}p)][ClO_4]_2$	Green			9.3 (9.45)	17.4 (17.2)
(8) $[Cu_2L^1(pz)][ClO_4]_2 \cdot H_2O$	Green			12.4 (12.25)	18.7 (18.5)
(9) $[Cu_2L^4][ClO_4]_2 \cdot H_2O$	Brown			7.75 (7.45)	17.15 (16.95)
(10a) $[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$	Green	37.4 (37.7)	4.15 (3.95)	7.55 (7.35)	16.5 (16.65)
(10b) $[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$	Green			6.85 (7.05)	16.2 (16.05)
(10c) $[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$	Green			6.35 (6.1)	13.65 (13.85)
(10d) $[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$	Green	43.25 (43.55)	4.0 (4.2)	6.75 (6.55)	15.0 (14.9)
(12) $[Cu_2L^6(OH)][ClO_4]_2 \cdot H_2O$	Green	28.4 (28.1)	4.7 (4.5)	8.85 (8.75)	20.0 (19.85)
(13) $[Cu_2L^6(OMe)][ClO_4]_2$	Blue-green			8.6 (8.8)	19.8 (19.95)
(14) $[Cu_2L^6(pz)][ClO_4]_2 \cdot H_2O$	Green			11.85 (12.15)	18.3 (18.4)
(15a) $[Cu_2L^7][ClO_4]_2 \cdot 2H_2O$	Green	37.1 (37.5)	4.2 (4.45)	7.0 (7.3)	16.45 (16.55)
(15b) $[Cu_2L^7][ClO_4]_2 \cdot 2H_2O$	Green			7.25 (7.05)	16.1 (15.95)
(15c) $[Cu_2L^7][ClO_4]_2 \cdot 2H_2O$	Green			6.75 (6.55)	15.0 (14.81)

[a] See Schemes 1 and 2 for structures. [b] Calculated values are given in parentheses.

Table 2. Infrared spectral data (cm^{-1}) for the dinuclear copper(II) complexes

Complex	ν(OH) Hydroxo	ν(OH) Aquo	ν(N–H)	ν(C=N)	ν(phenyl)	δ(N–H)	ν(C ··· O)
(3a)	3 540s	3 400br	3 300m 3 240w 3 220w	1 630s	1 610s	1 595m	1 550s
(3b)	3 540s	3 400br	3 320w 3 260w 3 130w	1 615s	1 600s	1 590s	1 540s
(3c)	3 540s	3 440br	3 320w 3 270w 3 220w 3 140w	1 605s	1 595s		1 530s
(4)	3 540s	3 440br	3 330w 3 265w 3 120w	1 620s	1 580s		1 535s
(5)	3 540s	3 440br	3 330w 3 260w 3 140w	1 635s	1 575s		1 545s
(6)			3 310w 3 220w 3 105w	1 625s	1 595s		1 550s
(7)			3 320w 3 220w 3 150w	1 630s	1 610s	1 595s	1 555s
(8)		3 460br	3 320w 3 240w 3 160w 3 100w	1 625s	1 610s	1 595s	1 550s
(9)			3 300w 3 220w 3 110w	1 620s	1 605s	1 595m	1 550s
(10a)		3 440br		1 635s	1 610m		1 565s
(10b)		3 400br		1 630s 1 620s	1 600s		1 550s 1 530s
(10c)		3 460br		1 630s 1 610s	1 605s		1 550s 1 535m
(10d)		3 400br		1 620s	1 595s		1 565s 1 545s
(12)	3 530s	3 400br	3 310m 3 260m 3 220w 3 160w		1 600m	1 580s	
(13)			3 320m 3 240m 3 150w		1 605s	1 590m	
(14)		3 400br	3 320w 3 300w 3 260w 3 210w 3 100w		1 600m	1 580m	
(15a)		3 440br	3 230m	1 630s	1 610s		1 560s
(15b)		3 440br	3 250m	1 620s	1 605s	1 570m	1 535s
(15c)		3 460br	3 230m	1 610s	1 580s		1 535s

absent, but a single N–H vibration is observed in the diazadiamino macrocyclic complexes (15a)—(15c) at *ca.* 3 230 cm^{-1}. The compounds (3a)—(3c), (4)—(9), and (10a)—(10c), which contain azomethine linkages, display a ν(C=N) vibration between 1 635 and 1 605 cm^{-1}. A characteristic difference between the complexes containing two or more azomethine linkages and tetra-amino linkages is the appearance of a strong band in the region 1 565—1 530 cm^{-1} in the former group of compounds. This is due to the ν(C ··· O) vibration of the phenol [27] which assumes partial double-bond character as a consequence of delocalisation of the double bonds in the chelate rings containing C=N linkages.

Electronic Spectra.—The electronic spectral features of the compounds are summarised in Table 3. In the visible region all of the complexes, except (10a), exhibit a single absorption band between 560 and 615 nm (ε = 115—245 $dm^3\ mol^{-1}\ cm^{-1}$). The position of this *d–d* band does not vary significantly in acetonitrile and Nujol mull. While a square-planar environment about the copper(II) ions appears to be certain in (10a)—(10d) the same conclusion may be drawn about the other complexes considering their similar spectral characteristics.

In the u.v. region the compounds (3)—(10) exhibit an intense absorption at *ca.* 355 nm. The absence of this band in the tetra-amino systems (12)—(14) and its reappearance in the diaminodiaza macrocyclic complexes (15a)—(15c) is a clear indication [28,29] of the origin of this band due to C=N chromophores (π–π* transition). In two cases, (7) and (8), an

Table 3. Electronic spectral data and magnetic moments for the dinuclear copper(II) complexes

Complex	Electronic spectral data [a] λ/nm (ε/dm³ mol⁻¹ cm⁻¹)	$\mu_{eff.}$/B.M. [b]
(3a)	590 (137), 363 (6 950); 580 [c]	0.67
(3b)	560 (150), 350 (7 250)	
(3c)	570 (165), 365 (8 230), 350 (8 200)	
(4)	590 (135), 363 (6 580)	1.20
(5)	590 (130), 363 (6 500)	1.27
(6)	590 (115), 355 (5 960); 580 [c]	0.74
(7)	590 (175), 355 (8 850), 380(sh) (7 360)	0.90
(8)	610 (190), 360 (7 320), 375(sh) (7 070)	1.08
(9)	600(sh) (215), 365 (9 770)	
(10a)	700(sh) (60), 600 (90), 350 (12 000)	0.68
(10b)	585 (137), 350 (13 370)	0.65
(10c)	580 (145), 350 (14 430)	
(10d)	580 (140), 350 (13 300)	0.66
(12)	585 (200), 330 (2 845), 290 (4 920)	1.66
(13)	590 (215), 330 (2 670), 290 (4 690); 600 [c]	1.68
(14)	615 (245), 410 (925), 330 (2 290)	1.15
(15a)	595 (200), 360 (8 345)	0.71
(15b)	580 (200), 355 (8 860)	0.76
(15c)	580 (190), 357 (8 280)	0.70

[a] In MeCN. [b] At 298 K. [c] Nujol mull.

additional shoulder at *ca.* 380 nm is observed which probably is another π–π* transition from a second chromophoric group in the molecules [*viz.* *p*-nitrophenolate in (7) and pyrazolyl in (8)]. The tetra-amino compounds (12) and (13) display two absorption maxima at 330 and 290 nm. The relatively weaker absorption at 330 nm appears to be due to ligand to metal (N→Cu) charge transfer which probably is swamped in (3)—(10) and (15) by the intense π–π* transition of the C=N groups. The strong absorption at 290 nm is most likely due to a phenyl-ring based π–π* transition.

Magnetic Moments.—It has been observed [1,2,4] in various hydroxo-bridged dicopper(II) complexes that the ground state is a triplet if the Cu–O–Cu bridge angle is less than 97.6°, and a singlet if it is greater than 97.6°. This observation has been rationalised theoretically [1-3] in the framework of the superexchange principle [30] involving a pathway for spin coupling of the two unpaired electrons in $d_{x^2-y^2}$ orbitals of each copper(II) ion and the *s* and *p* orbitals of the ligand oxygen. Available structural data show that the Cu–Cu separation in the dimers increases with the increase in Cu–O–Cu angle. It has been also indicated [31] that the antiferromagnetic interaction would decrease as electron density is removed from the bridging atoms. In the light of this information several useful conclusions have been drawn from the room-temperature magnetic moments (Table 3) of the compounds under discussion.

The magnetic moment of (3a) (0.67 B.M.) is considerably less than the values observed for (4) (1.20 B.M.) and (5) (1.27 B.M.). It may be noted that the azomethine linkage formed through 1,3-diaminopropane in (3a) offers more flexibility in the metal–ligand linkages which in turn lead to augmentation of the Cu–O–Cu bridge angle relative to the less flexible configurations in (4) and (5). Thus the stronger antiferromagnetic interaction expected for (3a) is consistent with the observed moments. If the moments of (3a), (6), and (7) are compared, the observed trend with respect to the bridged donor is OH ~ OMe < $OC_6H_4NO_2$-*p*. The magnetic moments of the other OH-bridged, (12), and OMe-bridged compounds, (13), are similar, however. The higher value found for (7) is due to the decreased electron density of the phenolic oxygen of

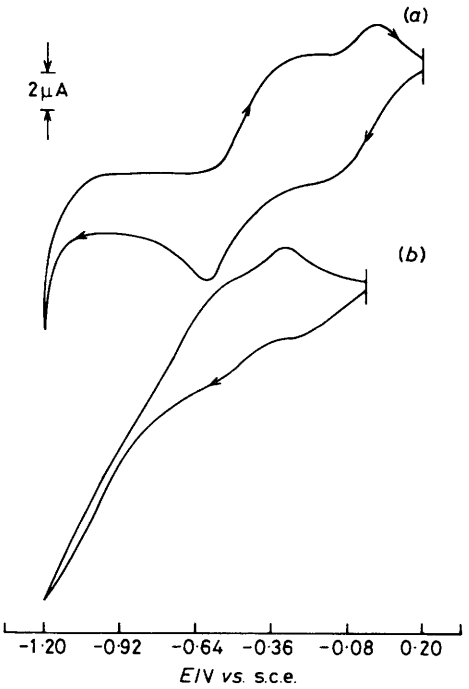


Figure 1. Cyclic voltammograms of acetonitrile solutions (~1 mmol dm⁻³) of (*a*) $[Cu_2L^1(OH)][ClO_4]_2 \cdot H_2O$ (3a) and (*b*) $[Cu_2L^6(OH)][ClO_4]_2 \cdot H_2O$ (12)

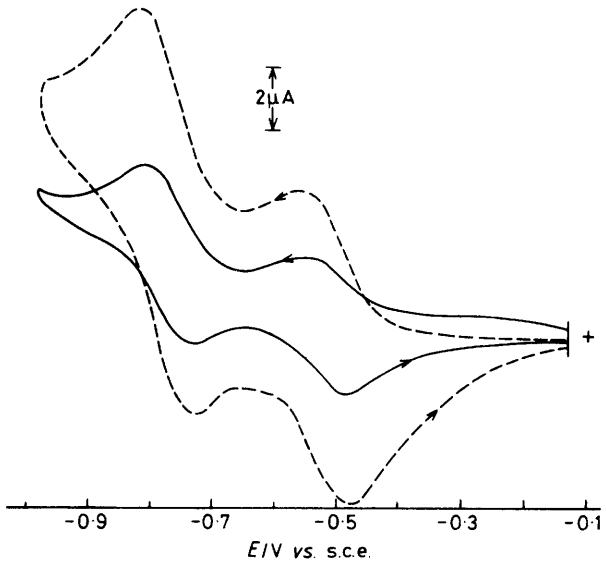


Figure 2. Cyclic voltammograms of $[Cu_2L^7][ClO_4]_2 \cdot 2H_2O$ (15a) in acetonitrile (~1 mmol dm⁻³) at scan rates of 100 (——) and 500 mV s⁻¹ (— — —)

$OC_6H_4NO_2$-*p* with respect to OH or OMe, which are about the same. When $OC_6H_4NO_2$-*p* is replaced by a *p*-cresol derivative, as in (10a), again the moment (0.68 B.M.) is equal to that of (3a). Thus by suitable choice of substituted phenols a useful correlation can be obtained between the *J* values and the calculated electron density of the phenols. Remarkably, the moments of (3a) and (6) are much less than those of their tetra-amino analogues, (12) and (13). This indicates that the Cu–O–Cu bridge angles in (12) and (13) are less than those

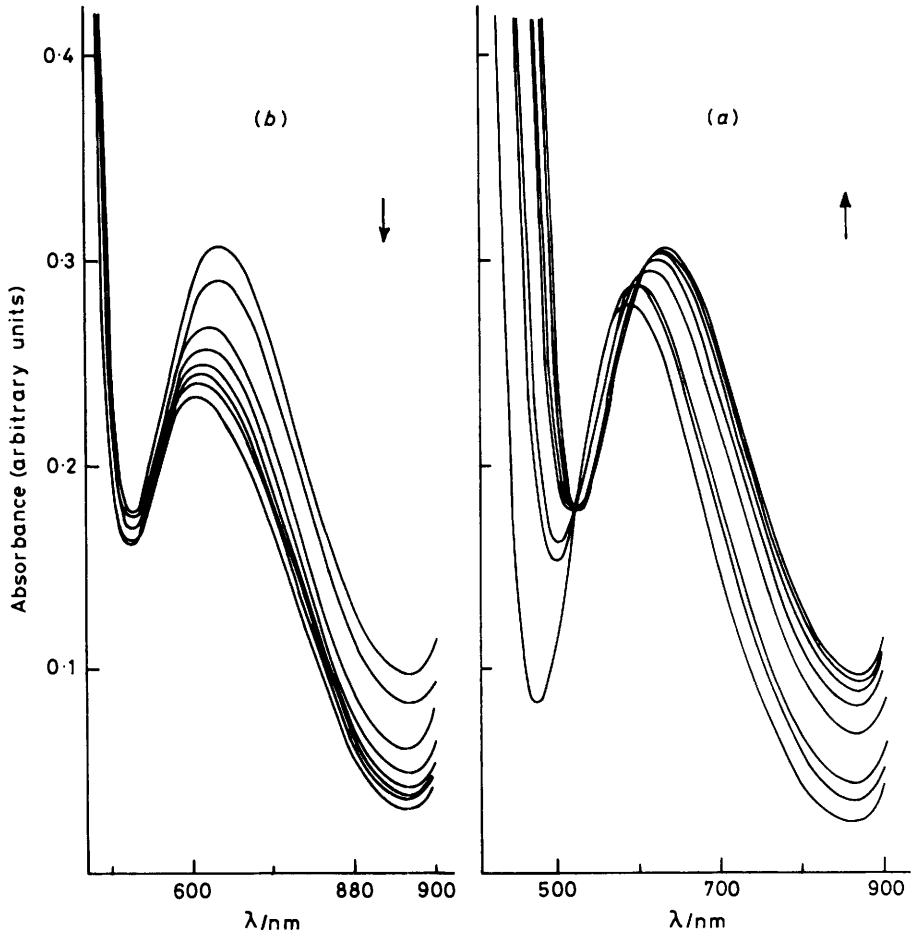


Figure 3. Kinetic spectra of a mixture of $[Cu_2L^1(OH)][ClO_4]_2 \cdot H_2O$ (3a) (2×10^{-3} mol dm^{-3}) and hmbdc (2×10^{-2} mol dm^{-3}) in acetonitrile. (*a*) Spectra recorded over first 50 min show the increase in band intensity with time. The lowest spectrum is of (3a) alone and the uppermost one was recorded after 50 min, which remained unchanged for another 10 min. (*b*) Spectra recorded up to 15 h after those in (*a*). The uppermost spectrum is the final spectrum in (*a*) and the lowest spectrum is that recorded after 15 h

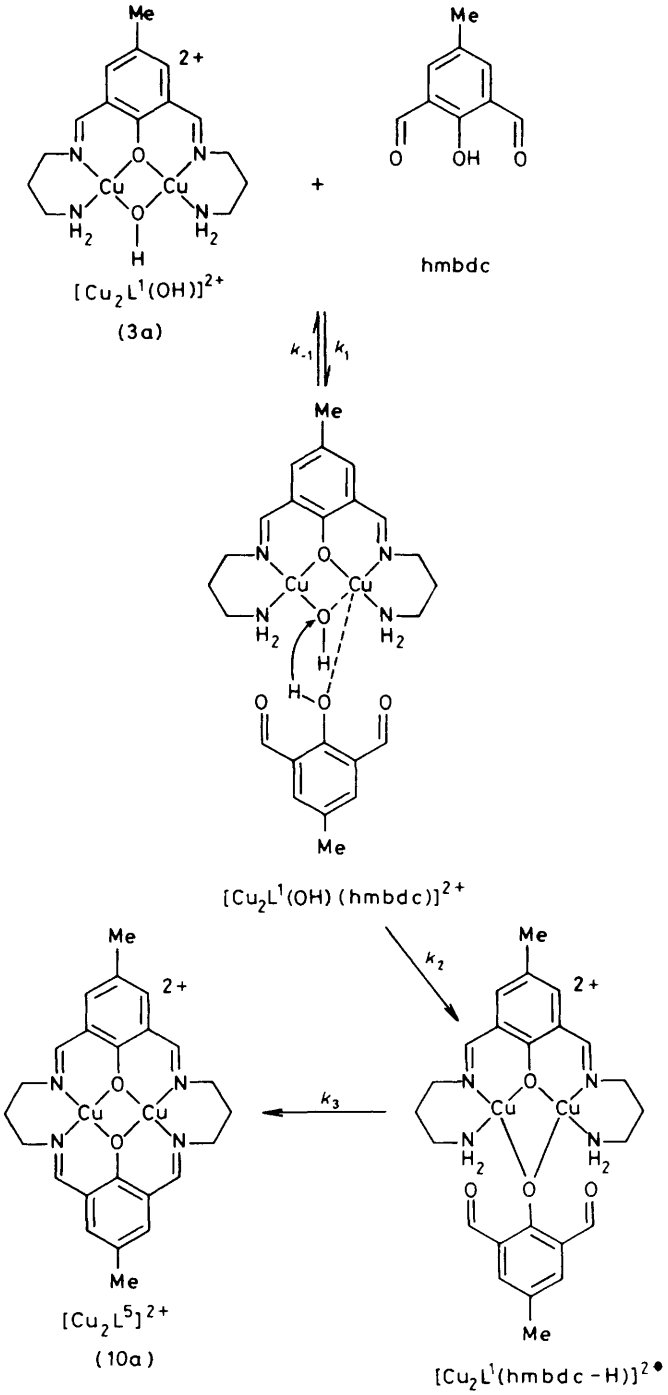
in (3a) and (6); the Cu–Cu separations in (12) and (13) are also shorter.

Electrochemistry.—The electrochemical behaviour of the hydroxo-bridged diazadiamino, (3a), and tetra-amino, (12), complexes and the diazadiamino macrocyclic complex (15a) were investigated in acetonitrile solution using a hanging mercury drop electrode (h.m.d.e.). The potentials were measured against a saturated calomel electrode (s.c.e.). The observed cyclic voltammograms (Figure 1) of (3a) and (12) reveal no evidence for the formation of either a stable mixed-valence (Cu^{II}/Cu^{I}) or stable binuclear Cu^{I} complex upon reduction. The voltammograms show two reduction waves in the potential range +0.2 to −0.8 V during the cathodic sweep, which at more negative potentials become very much distorted. In the anodic sweep broad non-Nernstian oxidation waves are obtained. The observed behaviour indicates that the dicopper(II) complexes are irreversibly reduced to Cu^{II}/Cu^{I} species, the latter rapidly undergoing decomposition. The electrochemical features of these two hydroxo-bridged compounds are similar to other hydroxo-bridged dicopper(II) complexes.[13,29]

Of greater interest are the redox properties of the macrocyclic complex (15a). We have already shown[27] that the mixed-valent $Cu^{II}Cu^{I}$ complexes of the tetra-aza macrocycles have considerably high stability in acetonitrile medium. The cyclic voltammograms of (15a) in acetonitrile (Figure 2) show that the electron transfers occur in two steps. At a scan rate of 100 mV s^{-1} the separation in peak potentials, ΔE_p ($E_{p.c} - E_{p.a.}$) for both the redox couples are 95 mV, and ΔE_p increases at higher scan rates, showing the quasi-reversible nature of the electron-transfer processes. The potentials of the two redox couples are −0.517 ($E^1 = Cu^{II}$–Cu^{II}/Cu^{II}–Cu^{I}) and −0.780 V ($E^2 = Cu^{II}$–Cu^{I}/Cu^{I}–Cu^{I}) *vs.* s.c.e. The difference between E^1 and E^2 can be used[19] to evaluate the conproportionation constant, $K_{con.}$, for reaction (i). For the species under consideration, $K_{con.}$ (2.8×10^4) is 20 times less than the corresponding value for the tetra-aza macrocyclic complex,

$$[Cu^{I}Cu^{I}L^7] + [Cu^{II}Cu^{II}L^7]^{2+} \overset{K_{con.}}{\rightleftharpoons} 2\,[Cu^{II}Cu^{I}L^7]^{+} \quad \text{(i)}$$

$[Cu^{II}Cu^{I}L^5]^+$ [from (10a)] in *NN*-dimethylformamide.[27] For the mixed-valent species of (10b)—(10d), $K_{con.}$ values (in acetonitrile) lie in the range[27] 2×10^9 to 1×10^{13} which are 5—9 orders of magnitude greater than the $K_{con.}$ of $[Cu^{II}Cu^{I}L^7]^+$. The results show that unlike the tetra-aza macrocycles the diazadiamino macrocycle does not stabilise the mixed-valent species significantly. It can be further stated, based on the arguments given earlier,[27] that there is a strong possibility that the odd electron is delocalised between the two copper centres.



Scheme 3.

Kinetic Studies.—It has been shown that the macrocyclic complexes $[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$ (10) can be synthesised by reacting $[Cu_2L^1(OH)][ClO_4]_2 \cdot nH_2O$ (3) with an appropriate aromatic aldehyde or ketone. We have investigated the mechanism of this reaction. Preliminary studies revealed that the formation of (10a) in acetonitrile medium can be conveniently followed spectrophotometrically. For the other substituted derivatives, the reaction rate is too slow. Figure 3(*a*) shows the spectral change that occurs on mixing (3a) (2×10^{-3} mol dm^{-3}) with hmbdc (2×10^{-2} mol dm^{-3}); there is an increase in intensity of the absorption maximum at 630 nm. The band intensity goes on increasing with time until it reaches the maximum value which is required, *ca.* 50 min.

Table 4. Variation of the pseudo-first-order rate constant ($k_{obs.}$) with change in concentration of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde (hmbdc) *

10^3[hmbdc]/mol dm^{-3}	$10^3 k_{obs.}$/s^{-1}
15	1.21
20	1.50
25	1.95
30	2.25
40	2.94
50	3.33

* $K = \frac{k_1}{k_{-1}} = 4.78$ mol dm^{-3}; $k_2 = 1.78 \times 10^{-2}$ s^{-1}.

After attaining the maximum absorbance the spectrum remains unchanged for *ca.* 10 min, and then the intensity reduces. The decrease in intensity of this band is shown in Figure 3(*b*). Unlike Figure 3(*a*), the spectral change occurring in Figure 3(*b*) is much slower and requires *ca.* 16 h to complete. The final spectrum becomes identical with an authentic specimen of (10a). Variation in the concentration of hmbdc has a pronounced effect on the rate of change occurring in Figure 3(*a*), but not on that in Figure 3(*b*).

On the basis of these experiments and also considering the formation of the phenoxo-bridged compound (7), the mechanism for the formation of (10a) is proposed to involve the pathways shown in Scheme 3. The spectral change observed in Figure 3(*a*) can be attributed to the formation of $[Cu_2L^1(hmbdc - H)]^{2+}$ and Figure 3(*b*) depicts the conversion of $[Cu_2L^1(hmbdc - H)]^{2+}$ to $[Cu_2L^5]^{2+}$. Evidence in support of the formation of $[Cu_2L^1(hmbdc - H)]^{2+}$ was obtained by noting a similar increase in band intensity as shown in Figure 3(*a*) by mixing a solution of (3a) with *p*-cresol.

The formation of $[Cu_2L^1(hmbdc - H)]^{2+}$ was followed under pseudo-first-order conditions using a 10—50-fold excess of hmbdc. In all cases good first-order plots were obtained. The variation of the observed rate constant ($k_{obs.}$) with the change in [hmbdc] is set out in Table 4. According to Scheme 3, applying the steady-state approximation,[32] equation (ii) is obtained, where $K = k_1/k_{-1}$. A good straight line fit has been obtained by plotting $k_{obs.}^{-1}$ against [hmbdc]$^{-1}$. The

$$k_{obs.} = \frac{k_2 K[\text{hmbdc}]}{1 + K[\text{hmbdc}]} \qquad \text{(ii)}$$

equilibrium constant, K, for the formation of $[Cu_2L^1(OH)(hmbdc)]^{2+}$ is 4.8 dm^3 mol^{-1} and $k_2 = 1.78 \times 10^{-2}$ s^{-1}.

The rate constant (k_3) for the cyclisation of $[Cu_2L^1(hmbdc - H)]^{2+}$ to $[Cu_2L^5]^{2+}$ is 7.4×10^{-5} s^{-1}. The result shows that the condensations of the two amino and aldehyde functions take place in a concerted fashion.

Acknowledgements

We are grateful to Professor T. P. Dasgupta of the University of West Indies, Jamaica for carrying out the electrochemical experiments.

References

1 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173.
2 J. A. Bertrand and P. G. Eller, *Prog. Inorg. Chem.*, 1976, **21**, 29.
3 O. A. Kahn, *Inorg. Chim. Acta*, 1982, **62**, 3.
4 M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259.
5 J. A. Fee, *Struct. Bonding (Berlin)*, 1975, **23**, 1.
6 H. Beinert, *Coord. Chem. Rev.*, 1980, **33**, 55.
7 E. I. Solomon, *Pure Appl. Chem.*, 1983, **55**, 1069.

8 K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensy, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 881.
9 T. N. Sorrell, M. R. Malachowski, and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 3252.
10 J. Birker, H. M. J. Hendriks, and J. Reedjk, *Inorg. Chim. Acta*, 1981, **55**, L17.
11 V. McKee, J. Dagdigian, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, 1981, **103**, 7000.
12 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 3228.
13 R. R. Gagne, R. P. Kreh, and J. A. Dodge, *J. Am. Chem. Soc.*, 1979, **101**, 6917.
14 Y. Nishida, K. Takahashi, H. Kuramoto, and S. Kida, *Inorg. Chim. Acta*, 1981, **54**, L103.
15 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.
16 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759.
17 S. E. Groh, *Isr. J. Chem.*, 1976, **15**, 277.
18 U. Casellato, P. Vigato, and M. Vidali, *Coord. Chem. Rev.*, 1977, **23**, 31.
19 R. R. Gagne, C. A. Koval, T. J. Smith, and M. C. Cimoline, *J. Am. Chem. Soc.*, 1979, **101**, 4571.
20 S. Lambert and D. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.
21 R. R. Gagne, L. M. Hemling, and T. J. Kistenmacher, *Inorg. Chem.*, 1980, **19**, 1226.
22 R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.
23 C. L. Spiro, S. L. Lambart, T. J. Smith, E. N. Duesler, R. R. Gagne, and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
24 R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513.
25 R. S. Drago, M. J. Desmond, B. B. Corden, and K. A. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 2287.
26 S. K. Mandal and K. Nag, *Inorg. Chem.*, 1983, **22**, 2567.
27 S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429.
28 I. E. Dickson and R. Robson, *Inorg. Chem.*, 1974, **13**, 1301.
29 J. J. Grzybowski, P. H. Merrell, and F. L. Urbach, *Inorg. Chem.*, 1978, **17**, 3078.
30 J. B. Goodenough, 'Magnetism and the Chemical Bond,' Interscience, New York, 1963.
31 P. J. Hay, J. C. Thibeault, and R. S. Hoffman, *J. Am. Chem. Soc.*, 1975, **97**, 4884.
32 R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon, Boston, 1974.

Received 24*th August* 1983; *Paper* 3/1497