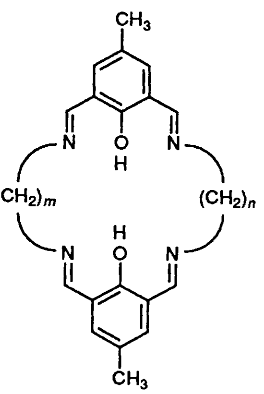
Template Synthesis of Copper(II)lead(II) Complexes of New Binucleating Macrocycles with Dissimilar Co-ordination Sites†

Makoto Tadokoro, Hiroshi Sakiyama, Naohide Matsumoto, Masahito Kodera, Hisashi Ōkawa* and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan

New binucleating macrocycles comprised of two molecules of 2,6-diformyl-4-methylphenol, a diamine (ethylenediamine or 1,3-propanediamine), and a diaminoalcohol (1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol) have been synthesised as copper(II)lead(II) complexes by 'stepwise' template reactions. The macrocycles possess two dissimilar co-ordination sites, a four-co-ordination N_2O_2 donor set and a five-co-ordination N_2O_3 set, sharing two bridging phenolic oxygens. The CuPb complex of the macrocycle with ethylenediamine and 1,3-diaminopropan-2-ol as the amine components has been structurally characterized by single-crystal X-ray analysis. The Cu^{II} is bound to the four-co-ordination site and has a planar configuration. The Pb^{II} is bound to the five-co-ordination site and assumes a seven-co-ordinate geometry with a unidentate perchlorate ion and a dimethylformamide molecule. In the macrocycles derived from 1,3-diaminopropan-2-ol the alcoholic oxygen can co-ordinate to Pb^{II} in both protonated and deprotonated forms, whereas in the macrocycles derived from 1,5-diaminopentan-3-ol the alcoholic oxygen co-ordinates to Pb^{II} in only the deprotonated form. Template synthesis of the macrocycle of 1,3-propanediamine and 1,5-diaminopentan-3-ol, using Cu^{II} and Ba^{II} as template ions, afforded a mononuclear copper(II) complex in which the five-co-ordination site of the macrocycle is occupied by a proton instead of Ba^{II}.

Macrocycles $H_2L^{m,n}$ comprised of two molecules of 2,6-diformyl-4-methylphenol and two diamines have been used extensively for the studies on homo- and hetero-binuclear and mixed-valence complexes.[1-7] Recently much effort has been made to modify the macrocycles by introducing potent donor groups on the lateral chains,[8-10] with the hope of increasing the number of co-ordination sites or of obtaining multinuclear complexes of desired structures. Macrocycles with the same lateral chains ($m = n$) may be synthesised in a one-pot reaction using a suitable metal ion as the template (direct template reaction). Unsymmetrical macrocycles with different lateral chains ($m \neq n$), however, cannot be synthesised by this method. The best way is a 'stepwise template reaction' which requires two kinds of metal ions in different stages in the cyclization reaction. In our previous study[11] a series of unsymmetrical macrocycles $H_2L^{m,n}$ ($m \neq n$) were prepared by the stepwise template reaction, using Cu^{2+} (or Ni^{2+}) and Pb^{2+} ions as the first and the second template ions, respectively. In this study the same method was applied for the synthesis of binucleating macrocycles containing an alcoholic group on one lateral chain as a potent donor. Four such macrocycles H_3L have been obtained as copper(II)lead(II) complexes one of which, $[CuPb(HL^1)][ClO_4]_2$·dmf (dmf = dimethylformamide), has been structurally characterized by single-crystal X-ray analysis. Of these macrocycles H_3L^2 was previously synthesised as dimanganese(II) complexes by Luneau *et al.*,[12] but the others are new.



$H_2L^{m,n}$

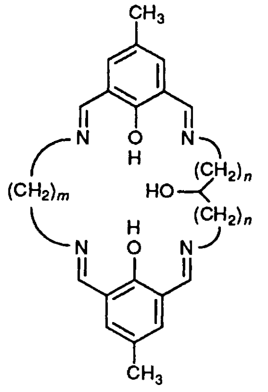
Experimental

Materials and Preparations.—2,6-Diformyl-4-methylphenol was prepared by the modified Duff reaction.[13] 1,3-Diaminopropan-2-ol was obtained commercially and 1,5-diaminopentan-3-ol was prepared by the method of Murase *et al.*[14] The precursor complexes, [*N,N'*-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) and [*N,N'*-bis(3-formyl-5-methylsalicylidene)propane-1,3-diaminato]copper(II), were obtained by the literature method.[2] Dimethylformamide, acetonitrile, methanol, tetrahydrofuran, ethyl acetate, and diethyl ether were purified in the usual ways.

$[CuPb(HL^1)][ClO_4]_2$·2dmf **1**. A suspension of *N,N'*-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) (1.0 g) in dmf (40 cm^3) and a dmf solution (20 cm^3) of $Pb(ClO_4)_2$·$3H_2O$ (1.11 g, 2.4 mmol) were mixed and refluxed with stirring. The addition of a dmf solution (40 cm^3) of 1,3-diaminopropan-2-ol (0.22 g, 2.4 mmol) resulted in a clear brown solution, which was evaporated to dryness to give a reddish brown solid. This was dissolved in acetonotrile (10 cm^3) and the solution was diffused with diethyl ether (*ca.* 3 cm^3) to give

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.
Non-SI unit employed: G = 10^{-4} T.



	m	n
H_3L^1	2	1
H_3L^2	3	1
H_3L^3	2	2
H_3L^4	3	2

red microcrystals. The complex was recrystallized from a dmf–ethyl acetate mixture. Yield after recrystallization 76%.

$[CuPb(HL^2)][ClO_4]_2$·dmf·MeCN **2**. A suspension of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)propane-1,3-diaminato]-copper(II) (1.00 g, 2.3 mmol) in dmf (40 cm^3) and a solution of $Pb(ClO_4)_2 \cdot 3H_2O$ (1.08 g, 2.3 mmol) in dmf (50 cm^3) were mixed and stirred at 50 °C to form a clear green solution. To the cooled solution was added a dmf solution (30 cm^3) of 1,3-diamino-propan-2-ol (0.21 g, 2.3 mmol), and the mixture was stirred at room temperature for 1 h then concentrated to dryness. The residue was dissolved in acetonitrile (10 cm^3) and the solution diffused with a large amount of ethyl acetate to give green crystals. Yield was 91%.

$[CuPbL^1]ClO_4 \cdot 2H_2O$ **3**. A suspension of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) (1.0 g, 2.4 mmol) in dmf (40 cm^3) was mixed with a dmf solution (20 cm^3) of $Pb(ClO_4)_2 \cdot 3H_2O$ (1.11 g. 2.4 mmol) and gently refluxed for 1 h with stirring. To this mixture were added successively a methanolic solution (20 cm^3) of 1,3-diaminopropan-2-ol (0.22 g, 2.4 mmol) and a methanolic sodium methoxide solution prepared by dissolving sodium (0.06 g) in methanol (20 cm^3), and the mixture was stirred at room temperature for 3 h to give reddish orange microcrystals. The complex was recrystallized from a dmf–tetrahydrofuran mixture.

$[CuPbL^2]ClO_4 \cdot 0.5H_2O$ **4**. A suspension of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)propane-1,3-diaminato]copper(II) (1.00 g, 2.3 mmol) and $Pb(ClO_4)_2 \cdot 3H_2O$ (1.08 g, 2.3 mmol) in dmf (50 cm^3) was stirred at 60 °C for 30 min. To this mixture were added successively a methanolic solution (20 cm^3) of 1,3-diaminopropan-2-ol (0.21 g, 0.23 mmol) and a methanolic solution of sodium methoxide solution prepared by dissolving sodium (0.1 g) in methanol (20 cm^3). The mixture was stirred at room temperature for 3 h to give yellowish green microcrystals. These were separated by filtration, washed successively with methanol and diethyl ether, and dried in air. Yield 91%.

$[CuPbL^3]Cl \cdot H_2O$ **5**. A suspension of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) (1.00 g, 2.4 mmol) and $Pb(ClO_4)_2 \cdot 3H_2O$ (1.11 g, 2.4 mmol) in methanol (60 cm^3) was refluxed for 15 min. To the chilled mixture was added a methanolic solution (30 cm^3) of 1,5-diaminopentan-3-ol dihydrochloride (0.66 g, 2.4 mmol) and the mixture was stirred at 40 °C for 15 min. Then an aqueous solution (10 cm^3) of sodium hydroxide (0.3 g) was added and the mixture refluxed for 1 h to give a brown precipitate, which was separated and washed with a small amount of water. A suspension of the product in dmf (100 cm^3) was allowed to stand at room temperature to give yellowish brown microcrystals. Yield 81%.

$[HCu(HL^4)]ClO_4 \cdot 0.5H_2O$ **6**. A solution of barium(II) perchlorate trihydrate (2.74 g, 7.0 mmol), 1,5-diaminopentan-3-ol dihydrochloride (1.92 g, 7.0 mmol), and triethylamine (2.2 g) in methanol (100 cm^3) was added dropwise to a suspension of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)propane-1,3-diaminato]copper(II) (3.00 g, 7.0 mmol) in methanol (50 cm^3). The resulting green solution was stirred for 1 h at room temperature to give green microcrystals. These were separated by filtration, washed successively with ethanol and diethyl ether, and recrystallized from an acetonitrile–ether mixture. Yield 92%.

Analytical data are summarized in Table 1.

X-Ray Structural Analysis of $[CuPb(HL^1)][ClO_4]_2$·dmf **1′**.—Single crystals of complex **1′** were grown from a dmf–tetrahydrofuran mixture as mono-dmf adducts. Reflection data were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo-Kα radiation at room temperature. Three standard reflections were monitored every 100 and showed no systematic decrease in intensity. The reflection data were corrected for Lorentz and polarization factors, but not for absorption and extinction effects. Unit-cell parameters were determined from 25 reflections ($20 < 2\theta < 30°$).

Crystal data. $C_{26}H_{31}Cl_2CuN_5O_{12}Pb$, $M = 947.2$, triclinic, space group $P\bar{1}$, crystal dimensions 0.3 × 0.4 × 0.3 mm, $a = 12.531(5)$, $b = 13.961(4)$, $c = 10.697(3)$ Å, $\alpha = 106.65(3)$, $\beta = 100.07(3)$, $\gamma = 102.38(3)°$, $D_c = 1.86$ g cm^{-3}, $Z = 2$, $U = 1694.48$ Å^3, $F(000) = 463$, μ(Mo-Kα) = 39.52 cm^{-1}, scan range $2.5 < 2\theta < 50°$, scan width $(1.2 + 0.35 \tan\theta)°$, octant measured ($+h$, $\pm k$, $\pm l$), number of reflections with $|F_o| > 3\sigma(|F_o|) = 4275$, $R = 0.0803$, $R' = 0.0854$.

The structure was solved by the standard heavy-atom method and refined by block-diagonal least squares, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with equal weights ($w = 1$) for all reflections. Hydrogen atoms bound to carbon were introduced in calculated positions. These hydrogen atoms were included in structure-factor calculations but not refined. Atomic scattering factors were taken from ref. 15. All computations were carried out on a FACOM M 780 computer at the Computer Centre of Kyushu University using a local version[16] of the UNICS III[17] and ORTEP[18] programs. The final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Other Physical Measurements.—Elementary analyses for C, H and N were obtained at the Elemental Analysis Service Center of Kyushu University. Copper analyses were made on a Shimadzu model AA-610 atomic absorption/flame emission spectrophotometer. Infrared spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls, electronic absorption spectra on a Shimadzu UV-210 spectrophotometer, ESR spectra on a JES-FE3X spectrometer, and fast atom bombardment (FAB) mass spectra on a JEOL JMS-DX300 mass spectrometer. Magnetic susceptibilities were measured on a Faraday balance at room temperature.

Results and Discussion

Preparations.—Success in template synthesis of macrocyclic complexes generally depends upon the choice of template metal ion.[19] Previous studies[9,11,19,20] suggest that non-transition-metal ions such as Pb^{2+} and Ba^{2+} can act as efficient template ions for the synthesis of various types of macrocycles. These metal ions are highly adaptable to the co-ordination cavity even when their ionic radii are not well matched with the size of the cavity. In the present synthesis of macrocycles H_3L^1–H_3L^4 the four-co-ordination site constructed from a simple diamine (ethylenediamine or 1,3-diaminopropane) was fixed with copper(II) ion as the first template ion and Pb^{II} or Ba^{II} was the second template ion which accommodates the

Table 1 Analyses of complexes **1**–**6** (calculated values in parentheses)

	Analysis (%)			
	C	H	N	Cu
1 $[\mathrm{CuPb(HL^1)}][\mathrm{ClO_4}]_2\cdot 2\mathrm{dmf}$	34.10 (34.15)	3.75 (3.75)	8.20 (8.25)	6.5 (6.2)
2 $[\mathrm{CuPb(HL^2)}][\mathrm{ClO_4}]_2\cdot 2\mathrm{dmf}\cdot\mathrm{MeCN}$	34.90 (34.75)	3.60 (3.60)	8.40 (8.40)	6.4 (6.4)
3 $[\mathrm{CuPbL^1}]\mathrm{ClO_4}\cdot 2\mathrm{H_2O}$	34.05 (34.10)	3.35 (3.35)	6.80 (6.90)	7.9 (7.9)
4 $[\mathrm{CuPbL^2}]\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$	36.25 (36.20)	3.25 (3.30)	7.15 (7.05)	7.5 (8.0)
5 $[\mathrm{CuPbL^3}]\mathrm{Cl}\cdot\mathrm{H_2O}$	39.65 (39.75)	3.80 (3.85)	7.75 (7.40)	8.4 (8.4)
6 $[\mathrm{HCu(HL^4)}]\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$	50.55 (50.40)	5.05 (5.20)	9.05 (9.05)	10.3 (10.3)

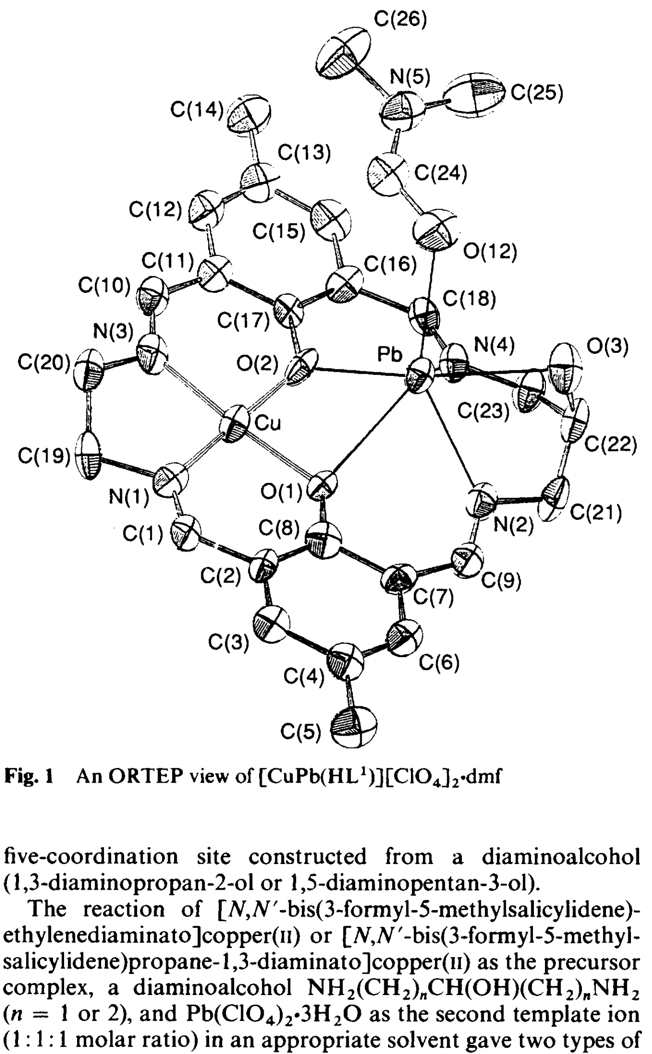


Fig. 1 An ORTEP view of $[\mathrm{CuPb(HL^1)}][\mathrm{ClO_4}]_2\cdot\mathrm{dmf}$

five-coordination site constructed from a diaminoalcohol (1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol).

The reaction of [*N,N'*-bis(3-formyl-5-methylsalicylidene)-ethylenediaminato]copper(II) or [*N,N'*-bis(3-formyl-5-methylsalicylidene)propane-1,3-diaminato]copper(II) as the precursor complex, a diaminoalcohol $\mathrm{NH_2(CH_2)}_n\mathrm{CH(OH)(CH_2)}_n\mathrm{NH_2}$ (n = 1 or 2), and $\mathrm{Pb(ClO_4)_2\cdot 3H_2O}$ as the second template ion (1:1:1 molar ratio) in an appropriate solvent gave two types of macrocyclic complexes $[\mathrm{CuPb(HL)}]^{2+}$ (L = $\mathrm{L^1}$ or $\mathrm{L^2}$) and $[\mathrm{CuPbL}]^+$ (L = $\mathrm{L^1}$–$\mathrm{L^3}$) as perchlorates or chlorides (Table 1). In these formulations HL^{2-} and L^{3-} denote the protonated and deprotonated forms of the macrocycles, respectively, with respect to the lateral alcohol group.

The macrocycles $\mathrm{H_3L^1}$ and $\mathrm{H_3L^2}$ formed both types of complexes depending upon the reaction conditions. The complexes $[\mathrm{CuPb(HL^1)}][\mathrm{ClO_4}]_2\cdot 2\mathrm{dmf}$ **1** and $[\mathrm{CuPb(HL^2)}][\mathrm{ClO_4}]_2\cdot\mathrm{dmf}\cdot\mathrm{MeCN}$ **2** were obtained without the use of any base, whereas $[\mathrm{CuPbL^1}]\mathrm{ClO_4}\cdot 2\mathrm{H_2O}$ **3** and $[\mathrm{CuPbL^2}]\mathrm{ClO_4}$ **4** were obtained when sodium methoxide was added as a base. The macrocycle $\mathrm{H_3L^3}$ was obtained as $[\mathrm{CuPbL^3}]\mathrm{Cl}\cdot\mathrm{H_2O}$ **5** when sodium hydroxide was added as a base.

The macrocycle $[\mathrm{HL^4}]^{2-}$ was isolated as the mononuclear copper(II) complex $[\mathrm{HCu(HL^4)}]\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$ **6** when barium ion was adopted as the second template ion. The five-co-ordination site of the macrocycle is probably occupied by a proton instead of Ba^{2+} based on elemental analyses and FAB mass spectra. The latter show a peak at *m/z* 510 which corresponds to $[\mathrm{Cu(HL^4)}]^+$.

It should be noted that the macrocycles $\mathrm{H_3L^1}$–$\mathrm{H_3L^3}$ form binuclear copper(II)lead(II) complexes whereas the macrocycles L^{2-} (in which the alcohol functionality is absent) form trinuclear $\mathrm{M^{II}Pb^{II}M^{II}}$ complexes $[\mathrm{Pb(ML)_2}]^{2+}$ (M = $\mathrm{Cu^{II}}$ or $\mathrm{Ni^{II}}$) where the lead(II) ion is sandwiched between two $\mathrm{ML}^{m,n}$ entities through the $\mathrm{N_2O_2}$ site of the $(\mathrm{CH_2})_n$ lateral chain. The X-ray structure analysis for complex **1'** (mono-dmf adduct) has demonstrated that the lateral alcoholic oxygen in the protonated form co-ordinates to the lead ion as discussed later. We presume a similar co-ordination of the alcoholic oxygen to the lead in the protonated form in complex **2** and in the deprotonated form in **3**–**5**.

Crystal Structure of Complex **1'**.—An ORTEP view of the complex cation $[\mathrm{CuPb(HL^1)}]^{2+}$ is shown in Fig. 1, together with the atom numbering scheme. Relevant bond distances and angles are given in Table 3.

The crystal is comprised of the complex cation $[\mathrm{CuPb(HL^1)}]^{2+}$, two perchlorate ions, and a dmf molecule. The copper(II) ion is bound to the four-co-ordination site which assumes a nearly planar structure with two phenolic oxygens and two imino nitrogens. The Cu–N and Cu–O bond lengths are similar to those of [*N,N'*-bis(salicylidene)ethylenediaminato]copper(II).[21]

The lead(II) ion is bound to the five-co-ordination site constructed from 1,3-diaminopropan-2-ol. The alcoholic oxygen O(3) on the lateral chain co-ordinates to the Pb in the protonated form with Pb–O 2.61(2) Å. The bond lengths from the lead to the phenolic oxygens and imino nitrogens fall in the range 2.44(1)–2.57(2) Å, which are short compared with corresponding values of the related CuPbCu complex[11] of $(\mathrm{L}^{3,3})^{2-}$ [2.49(1)–2.71(2) Å]. The deviation of the Pb from the least-squares plane defined by the phenolic oxygens and imino nitrogens (1.48 Å) is larger than that (1.28 Å) of the dilead(II) complex of $(\mathrm{L}^{3,3})^{2-}$.[22] The open face of the lead co-ordination sphere is occupied by a dmf oxygen O(12) at 2.60(1) Å, affording a six-co-ordinate geometry. One perchlorate ion weakly interacts with lead [Pb ··· O(10) 2.99(3) Å], whereas another is free from co-ordination and captured in the crystal lattice. The Pb ··· Cu separation is 3.344(3) Å.

General Properties.—The complexes **1**–**5** are stable in the solid state and even in solution (dmf, methanol). On the other hand, **6** is unstable in solution, especially when heated, and undergoes disproportionation to form a binuclear copper(II) complex $[\mathrm{Cu_2L^{3,3}}]^{2+}$ first obtained by Pilkington and Robson[1] by direct tempelate reaction.

Complexes **1**–**6** show no IR bands due to amino or aldehyde groups. Instead, they show an intense vibration around 1620 $\mathrm{cm^{-1}}$ attributable to the C=N group. Complex **6** exhibits another band at 1650 $\mathrm{cm^{-1}}$ which may be attributed to the C=N group in the five-co-ordination site[2] occupied by a proton. For **1** and **2** the ν(OH) vibration of the alcoholic group appears around 3400 $\mathrm{cm^{-1}}$ (Nujol mulls). The presence of water in **3**–**6** is evidenced by a broad vibration near 3400 $\mathrm{cm^{-1}}$. The presence of

Table 2 Atomic coordinates (× 10^4) of non-hydrogen atoms in complex **1′**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb	1925(1)	525(1)	18(1)	C(16)	1787(18)	−1294(13)	−3298(18)
Cu	3906(2)	−706(2)	416(2)	C(17)	2381(16)	−1470(13)	−2217(17)
O(1)	4017(11)	740(9)	1035(13)	C(18)	1655(18)	−250(15)	−3293(18)
O(2)	2881(12)	−736(8)	−1110(13)	C(19)	5191(20)	−1670(16)	1804(21)
O(3)	867(14)	1786(12)	−686(15)	C(20)	4164(20)	−2540(15)	844(21)
N(1)	4910(15)	−660(11)	1968(17)	C(21)	2700(22)	2935(15)	−233(22)
N(2)	3150(15)	2338(12)	543(16)	C(22)	1637(20)	2319(14)	−1305(20)
N(3)	3663(15)	−2199(12)	−230(16)	C(23)	1775(20)	1498(15)	−2525(20)
N(4)	1902(14)	544(12)	−2268(15)	Cl(1)	3441(6)	−5688(4)	−2778(7)
C(1)	5340(18)	70(14)	3063(20)	O(4)	3700(20)	−6623(13)	−2890(25)
C(2)	5177(17)	1129(13)	3249(19)	O(5)	3592(24)	−5361(19)	−3877(28)
C(3)	5708(19)	1853(15)	4510(19)	O(6)	4166(26)	−4959(19)	−1601(28)
C(4)	5643(19)	2906(15)	4835(20)	O(7)	2286(21)	−5853(24)	−2858(33)
C(5)	6257(22)	3704(17)	6195(22)	Cl(2)	−2015(5)	1112(4)	−2708(6)
C(6)	5051(19)	3148(15)	3843(20)	O(8)	−2210(20)	2060(15)	−2759(21)
C(7)	4486(17)	2448(14)	2578(19)	O(9)	−920(16)	1080(18)	−2899(21)
C(8)	4556(18)	1361(15)	2242(19)	O(10)	−2003(20)	1018(19)	−1450(22)
C(9)	3892(18)	2839(14)	1633(20)	O(11)	−2851(18)	314(18)	−3769(25)
C(10)	3053(18)	−2824(15)	−1371(19)	O(12)	18(14)	−795(12)	−1474(16)
C(11)	2445(18)	−2530(14)	−2399(19)	N(5)	−1142(17)	−2350(14)	−2951(18)
C(12)	1841(20)	−3314(15)	−3608(21)	C(24)	−328(21)	−1812(17)	−1940(23)
C(13)	1233(20)	−3150(16)	−4695(21)	C(25)	−1749(27)	−1895(23)	−3785(27)
C(14)	605(23)	−3989(18)	−5973(23)	C(26)	−1457(30)	−3473(20)	−3356(32)
C(15)	1205(19)	−2119(17)	−4521(19)				

Table 3 Selected interatomic dimensions (bond lengths in Å, angles in °) for $[CuPb(HL^1)][ClO_4]_2$·dmf **1′**

Lead environment			
Pb ••• Cu	3.344(3)	Pb–N(4)	2.45(2)
Pb–O(1)	2.57(1)	Pb–O(3)	2.61(2)
Pb–O(2)	2.49(1)	Pb ••• O(10)	2.99(3)
Pb–N(2)	2.51(2)	Pb–O(12)	2.60(1)
Copper environment			
Cu–O(1)	1.90(1)	Cu–N(1)	1.88(2)
Cu–O(2)	1.88(1)	Cu–N(3)	1.93(2)
Lead environment			
O(1)–Pb–O(2)	60.1(4)	O(12)–Pb–O(2)	87.6(5)
O(1)–Pb–N(4)	102.9(5)	O(12)–Pb–O(3)	79.6(5)
O(2)–Pb–N(4)	69.5(6)	O(12)–Pb–N(2)	143.1(6)
O(2)–Pb–N(2)	108.7(5)	O(12)–Pb–N(4)	75.3(5)
N(2)–Pb–O(1)	67.3(5)	O(10)–Pb–O(1)	72.6(5)
N(2)–Pb–N(4)	79.9(5)	O(10)–Pb–O(2)	71.3(6)
O(3)–Pb–O(1)	132.6(4)	O(10)–Pb–O(3)	147.6(6)
O(3)–Pb–O(2)	135.4(5)	O(10)–Pb–N(2)	131.5(5)
O(3)–Pb–N(2)	65.4(5)	O(10)–Pb–N(4)	136.3(6)
O(3)–Pb–N(4)	65.9(6)	O(10)–Pb–O(12)	80.0(6)
O(12)–Pb–O(1)	144.9(5)		
Copper coordination			
O(1)–Cu–O(2)	84.3(5)	O(2)–Cu–N(3)	93.1(6)
O(1)–Cu–N(1)	94.8(6)	O(2)–Cu–N(1)	178.6(8)
O(1)–Cu–N(3)	175.3(7)	N(1)–Cu–N(3)	87.7(7)

acetonitrile in **2** is supported by a sharp band near 2100 cm^{-1}. Complexes **1** and **2** should show a ν(C=O) vibration at around 1650 cm^{-1} for the dmf but this is probably obscured by the intense C=N vibration.

Electronic spectral data for complexes **1**–**6** are summarized in Table 4. Each complex shows an intense absorption band near 390 nm which may be assigned to the π–π* transition of the azomethine group.[23] The absorption band at 530–603 nm is assigned to a d–d transition of copper(II). The band for **1**, **3** and **5** (532–562 nm) is located at a shorter wavelength relative to that for **2**, **4** and **6** (590–600 nm). In the former complexes the four-co-ordination site is comprised of ethylenediamine and exerts a strong ligand field compared with that constructed from 1,3-diaminopropane in the latter complexes.[2]

Table 4 Electronic spectral data in dmf and magnetic moments at room temperature

Complex	λ_{max}(ε/dm^3 mol^{-1} cm^{-1})		μ_{eff}/μ_B
1	378 (15 500)	532 (142)	1.84
2	377 (11 400)	590 (32)*	1.78
3	389 (18 100)	536 (221)	1.80
4	387 (14 200)	590 (73)*	1.80
5	400 (10 000)	562 (254)	1.84
6	400 (12 600)	603 (126)	1.82

* Broad peak.

The magnetic moments of the complexes fall in the range 1.78–1.84 μ_B per molecule (see Table 4) which are common for copper(II). The X-band ESR spectra of the complexes except for **5**, in dmf at room temperature, show an isotropic signal with a four-line hyperfine structure due to copper ($I = \frac{3}{2}$). A typical spectrum is shown in Fig. 2(*a*). The ESR parameters determined are g_{iso} = 2.07–2.10 and A_{iso} = 70–90 G. Spectra for **5** could not be measured in solution because of its very low solubility in most solvents.

When measured in frozen dmf solutions the complexes **2** and **4** showed an axial pattern ($g_{\parallel} = 2.24$, $A_{\parallel} = 170$ G and $g_{\perp} = 2.06$ for **2**; $g_{\parallel} = 2.24$, $A_{\parallel} = 172$ G and $g_{\perp} = 2.06$ for **4**). The spectrum of **2** is given in Fig. 2(*b*). On the other hand, complex **1** showed a complicated spectrum [Fig. 2(*c*)] with some intense signals in the range 2900–3500 G and weaker signals at 1600 and 2600 G. The most noticeable is a signal at 1600 G which shows a seven-line hyperfine structure with a coupling constant of *ca.* 85 G. This value is about one half those for monomeric copper(II) complexes[24] and comparable to that of the spin-triplet state of binuclear copper(II) complexes.[25–27] The weak signal at 2600 G also exhibits a seven-line hyperfine structure with a coupling constant of *ca.* 90 G. Thus, we may conclude that the ESR signals for **1** [Fig. 2(*c*)] arise from a spin-triplet state of a dimeric species produced by the out-of-plane bonding between CuN_2O_2 entities, as demonstrated for [*N*,*N*′-disalicylideneethylenediaminato]copper(II).[28–30] Such a dimerization was also detected for the trinuclear $Cu^{II}Pb^{II}Cu^{II}$ complexes of

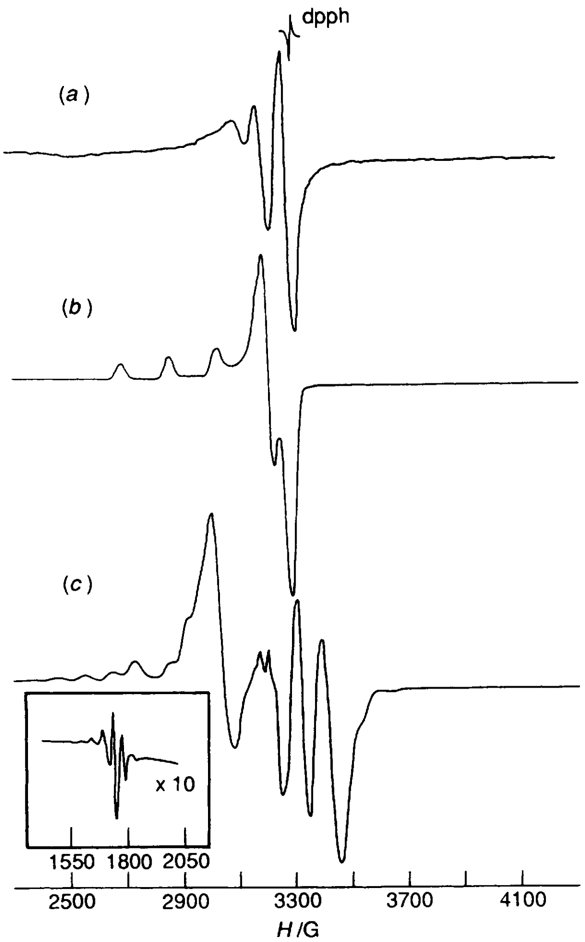


Fig. 2 The ESR spectra of (*a*) complex **4** in dmf at room temperature, (*b*) **2** in a frozen dmf solution at liquid-nitrogen temperature, and (*c*) **1** in a frozen dmf solution at liquid-nitrogen temperature. dpph = Diphenylpicrylhydrazyl

L^{2-}.[11] The ESR spectrum of complex **6** in frozen dmf solution is essentially of axial pattern but a multi-line structure is superposed on the $g_{\parallel}$ component, suggesting that both mono- and di-meric species coexist in this case.

References

1 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.
2 H. Ōkawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 751; *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759.
3 B. F. Hoskins, R. Robson and G. A. Williams, *Inorg. Chim. Acta*, 1976, **16**, 121; B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2593, 2607.
4 A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899.
5 R. R. Gagne, C. A. Koval and T. J. Smith, *J. Am. Chem. Soc.*, 1977, **99**, 8367; R. R. Gagne, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571; 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; C. L. Spiro, S. E. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
6 R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513; S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.
7 S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429; 1984, 2141; S. K. Mandal, B. Adhikary and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1986, 1175.
8 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 1334; *Inorg. Chem.*, 1989, **28**, 2902.
9 S. S. Tandon and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1989, 19.
10 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1987, 1852; B. F. Hoskins, R. Robson and P. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 488.
11 M. Tadokoro, H. Ōkawa, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1991, 1657.
12 D. Luneau, J. Savariault, P. Cassoux and J. Tuchagues, *J. Chem. Soc., Dalton Trans.*, 1988, 1225.
13 A. Denton and H. Suschitzky, *J. Chem. Soc.*, 1963, 4741.
14 I. Murase, M. Hatano, M. Tanaka, S. Ueno, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2404.
15 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
16 S. Kawano, *Rep. Comput. Cent., Kyushu Univ.*, 1980, **13**, 39.
17 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, 1979, **55**, 69.
18 C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
19 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461.
20 H. Adams, N. A. Bailey, D. E. Fenton, R. J. Good, R. Moody and C. O. Rodriguez de Barbarin, *J. Chem. Soc., Dalton Trans.*, 1987, 207.
21 E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. A*, 1970, 400, 406.
22 M. Tadokoro, H. Sakiyama, N. Matsumoto, H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3337.
23 B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627.
24 For example, Y. Nonaka, T. Tokii and S. Kida, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 312.
25 G. F. Kokoszka, M. Linzer and G. Gordon, *Inorg. Chem.*, 1968, **7**, 1730.
26 R. W. Duerst, S. J. Baum and G. F. Kokoszka, *Nature (London)*, 1969, **222**, 665.
27 T. Kamiusuki, H. Ōkawa, E. Kitaura, M. Koikawa, H. Matsumoto, H. Oshio and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1989, 2077.
28 D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
29 M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, 1946, **68**, 2267.
30 G. O. Carlisle and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 633.

Received 29*th July* 1991; *Paper* 1/03892C