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CHARACTERIZATION OF REACTION PRODUCTS OF SEVERAL BIS(β-DIKETONATO)COPPER(II) COMPOUNDS WITH 1H-PYRAZOLES. ADDUCTS, DI- AND TETRANUCLEAR COMPLEXES, AND COORDINATION POLYMERS

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Abstract—When $[Cu(L^1)_2]$ (HL^1 = aliphatic β-diketone with branched alkyl groups) and $[Cu(L^2)_2]$ (HL^2 = aliphatic β-diketone with linear alkyl groups) were allowed to react with 1H-pyrazoles (Hpzl), tetranuclear complexes $[Cu_4(\mu_4\text{-}O)(L^1)_4(\mu\text{-pzl})_2]$ and dinuclear complexes $[Cu_2(L^2)_2(\mu\text{-pzl})_2]$ were produced respectively, but the reactions of $[Cu(L^3)_2]$ (HL^3 = aroyl- or heteroaroylacetone) with 1H-pyrazole (Hpz) gave coordination polymers $[\{Cu(L^3)(\mu\text{-pz})\}_n]$ and/or adducts $[Cu(L^3)_2\ (Hpz)_n]$ (n = 1 and/or 2). The substituent effects of the β-diketonato ligands on the reaction products are discussed. The structure of one of the tetranuclear products $[Cu_4(\mu_4\text{-}O)(dibm)_4(\mu\text{-4-mpz})_2]$ (Hdibm = 2,6-dimethylheptane-3,5-dione; 4-Hmpz = 4-methyl-1H-pyrazole) has been determined by X-ray analysis. The structures of some of the other products are estimated on the basis of their IR and diffuse reflectance spectra.

Many investigations have been reported on the reactions of $[Cu(L)_2]$ (HL = β-diketone) with nitrogen bases[1,2] including 1H-pyrazoles.[3–6] As two types of nitrogen atoms, pyridine- and pyrrole-types (imino group), are present in a molecule, 1H-pyrazole can form both pyrazole and pyrazolato complexes of various kinds.[7] In our extensive studies we have observed that the reaction products of $[Cu(L)_2]$ with 1H-pyrazoles are considerably affected by the structure of L. For example, the reactions of $[Cu(L)_2]$ with 1H-pyrazole (Hpz) gave dinuclear

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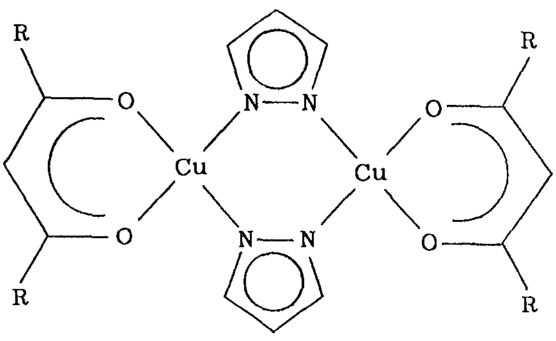
complexes $[Cu_2(L)_2(\mu\text{-pz})_2]$ where HL is an aliphatic β-diketone with linear alkyl groups, while 1 : 1 adducts $[Cu(L)_2(Hpz)]$ were produced when HL was an aroyl- or heteroaroylacetone.[3]



Dinuclear complex $[Cu_2(L)_2(\mu\text{-pz})_2]$

In order to discuss these reactions clearly, we have classified the ligands HL into three groups according to the reaction characteristics of $[Cu(L)_2]$; HL^1 and HL^2 = aliphatic β-diketones with branched and linear alkyl groups, respectively, and HL^3 = aroyl- or heteroaroylacetone. These reactions are very different from those of $[Cu(hfac)_2]$ (Hhfac = 1,1,1,5,5,5-hexafluoropentane-2, 4-dione) with 1H-pyrazoles which we have studied previously.[4–6]

Here we report the general trends in the reaction products corresponding to the structures of the reactant $[Cu(L)_2]$, as well as the structures and spectral characterization of the products, namely tetranuclear complexes $[Cu_4(\mu_4\text{-O})(L^1)_4(\mu\text{-pzl})_2]$, dinuclear complexes $[Cu_2(L^2)_2(\mu\text{-pzl})_2]$ (Hpzl = 1H-pyrazoles), coordination polymers $[\{Cu(L^3)(\mu\text{-pz})\}_n]$ and adducts $[Cu(L^3)_2(Hpz)_n]$ (n = 1 and/or 2).

EXPERIMENTAL

Materials

The β-diketones employed were 2,2,6,6-tetramethylheptan-3,5-dione (Hdpm), 2,6-dimethylheptan-3,5-dione (Hdibm), nonan-4,6-dione (Hdnbm), heptan-3,5-dione (Hdprm), pentan-2,5-dione (Hacac), 1-phenylbutan-1,3-dione (Hbzac), 1-(2-thienyl)-butan-1,3-dione (Htac), 1-(2-furyl)-butan-1,3-dione (Hfac), 4,4,4-trifluoro-1-phenylbutan-1,3-dione (Htfbzac), 4,4,4-trifluoro-1-(2-thienyl)-butan-1,3-dione (Htftac) and 4,4,4-trifluoro-1-(2-furyl)-butan-1,3-dione (Htffac), respectively, and their copper(II) complexes $[Cu(L)_2]$ were prepared by the reported method.[3] 1H-Pyrazole (Hpz) and 3,5-dimethyl-1H-pyrazole (3,5-Hdmpz) (Aldrich Chemical Co.) were recrystallized from light petroleum (boiling point range 30–70°C). 3-Methyl-1H-pyrazole (3-Hmpz) and 4-methyl-1H-pyrazole (4-Hmpz) (Aldrich Chemical Co.) were used without further purification.

Preparation of the complexes

$[Cu_4(\mu_4\text{-O})(dpm)_4(\mu\text{-pz})_2]$ (**1t**) *and* $[Cu_4(\mu_4\text{-O})(dibm)_4(\mu\text{-pz})_2]$ (**2t**). $[Cu(dpm)_2]$ or $[Cu(dibm)_2]$ was dissolved in ethanol with an equimolar quantity of 1H-pyrazole. The solution was boiled under reflux for several hours. After standing for a few weeks, a bluish violet precipitate (**1t** or **2t**) was formed. It was filtered off and dried *in vacuo*. The complex **1t** or **2t** was also obtained from the filtrate added to an aqueous solution of copper(II) acetate monohydrate.

$[Cu(dibm)(4\text{-mpz})(4\text{-Hmpz})]$ (**4s**) *and* $[Cu_4(\mu_4\text{-O})(dibm)_4\ (\mu\text{-4-mpz})_2]$ (**3t**). $[Cu(dibm)_2]$ was dissolved in light petroleum containing a small amount of acetone with twice molar quantities of 4-methyl-1H-pyrazole. The solution was boiled under reflux for 1 h. After the solvent was evaporated at room temperature, a dark violet residue (**4s**) was obtained. After **4s** was recrystallized from light petroleum, bluish violet crystals with a different composition (**3t**) were obtained, which were filtered off and dried *in vacuo*.

$[Cu_2(dnbm)_2(\mu\text{-3-mpz})_2]$ (**5d**), $[Cu_2(dnbm)_2(\mu\text{-4-mpz})_2]$ (**6d**) *and* $[Cu_2(dnbm)_2(\mu\text{-3,5-dmpz})_2]$ (**7d**). These complexes were prepared by a similar method to that reported for $[Cu_2(dnbm)_2\ (\mu\text{-pz})_2]$.[3]

$[Cu_2(dnbm)_2(\mu\text{-pz})_2]$ (**8d**), $[Cu_2(dprm)_2(\mu\text{-pz})_2]$ (**9d**) *and* $[Cu_2(acac)_2(\mu\text{-pz})_2]$ (**10d**). These complexes were prepared by the reported method.[3]

$[\{Cu(tac)(\mu\text{-pz})\}_n]$ (**11p**) *and* $[\{Cu(fac)(\mu\text{-pz})\}_n]$ (**12p**). $[Cu(tac)_2]$ or $[Cu(fac)_2]$ was dissolved in cyclohexane containing a small amount of acetone with a small excess of 1H-pyrazole. The solution was boiled under reflux for several hours. After standing for a few days, a dark brown precipitate (**11p** or **12p**) was formed, which was filtered off and dried *in vacuo*.

$[\{Cu(tfbzac)(\mu\text{-pz})\}_n]$ (**13p**) *and* $[Cu(tfbzac)_2(Hpz)]$ (**16a**). $[Cu(tfbzac)_2]$ was dissolved in cyclohexane containing a small amount of acetone with an equimolar quantity of 1H-pyrazole. The solution was boiled under reflux for several hours. After standing for a few days, a purplish blue precipitate (**13p**) was formed, which was filtered off and dried *in vacuo*. The adduct **16a** was obtained as pale green crystals from the filtrate.

$[\{Cu(tftac)(\mu\text{-pz})\}_n]$ (**14p**), $[\{Cu(tffac)(\mu\text{-pz})\}_n]$ (**15p**), $[Cu(tftac)_2(Hpz)]$ (**17a**) *and* $[Cu(tffac)_2(Hpz)]$ (**18a**). $[Cu(tftac)_2]$ or $[Cu(tffac)_2]$ was dissolved in cyclohexane containing a small amount of acetone with an excess of 1H-pyrazole. The solution was boiled under reflux for several hours. After standing for a few days, light green or green crystals (**17a** or **18a**) were formed, which were filtered off and dried *in vacuo*. The coordination polymer (**14p** or **15p**) was obtained as a purplish black precipitate from the filtrate.

$[Cu(tac)_2(Hpz)_2]$ (**19b**) *and* $[Cu(fac)_2(Hpz)_2]$ (**20b**). $[Cu(tac)_2]$ or $[Cu(fac)_2]$ was dissolved in cyclohexane containing a small amount of acetone with a small excess of twice molar quantities of 1H-pyrazole. The solution was boiled under reflux for several hours. After standing for a few days, dark green crystals (**19b** or **20b**) were formed, which were filtered off and dried *in vacuo*.

Spectral measurements

The diffuse reflectance spectra were recorded on a Jasco Ubest 55 spectrophotometer and IR spectra on a Nicolet 5ZDX Fourier-transform spectrometer.

X-ray crystallographic analysis of 3t

The X-ray diffraction data were collected by the use of an automated four-circle diffractometer, Mac Science MXC18, with graphite-monochromated Cu-K_α radiation (λ = 1.54178 Å) up to $2\theta = 120^\circ$, with the 2θ–ω scan technique. Three standard reflections were monitored after every 100 reflections. No decomposition of the crystal was observed. The usual corrections for Lorentz and polarization effects were made, but no absorption correction was applied.

For the structure determination, 6778 independent reflections were used. Calculations were carried out on a Sun3/80 computer using the Monte Calro–Maltan direct method[8] and ORTEP programs.[9] The atomic scattering factors, including the anomalous scattering factors, were taken from Ref. 10. The positions of all the hydrogen atoms were determined from the difference Fourier map.

Crystallographic data and experimental details: $C_{44}H_{70}N_4O_9Cu_4$, $M = 1053.24$, triclinic, $P\bar{1}$, $a = 9.706(5)$, $b = 13.467(4)$, $c = 20.724(6)$ Å, $\alpha = 90.52(3)$, $\beta = 103.18(3)$, $\gamma = 91.75(3)^\circ$, $V = 2636(1)$ Å^3, $Z = 2$, $D_c = 1.327$ Mg m^{-3}, crystal size = $0.50 \times 0.30 \times 0.15$ mm^3, $F(000) = 1100$, $\mu(\text{Cu-}K_\alpha) = 21.85$ cm^{-1}. The final discrepancy factors were $R = 0.046$, and $R_w = 0.051$ ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ (unit weights), $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/|\sigma(F)|^2$).

Supplementary material (atomic coordinates, remaining bond lengths and angles, and thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Preparation

Classification and abbreviation of the β-diketones and their copper(II) complexes employed are shown in Table 1. The reaction products of $[Cu(L^1)_2]$ and $[Cu(L^2)_2]$ with 1H-pyrazoles are shown in Table 2. They are all tetra- or dinuclear complexes, except for the complex **4s**. On the other hand, the reaction products of $[Cu(L^3)_2]$ with 1H-pyrazole are coordination polymers and/or adducts, and they are shown in Table 3. Characterization of the complexes was made by microanalysis, IR and UV spectroscopies. Here the notation **p**, **t**, **d**, **s**, and **a** (or **b**) denotes polymers, tetra- and dinuclear complexes, substituted complex and adducts, respectively.

Crystal structure

A perspective view of **3t** is shown in Fig. 1 with the atomic numbering. The geometry of the metal

Table 1. Classification and abbreviation of the β-diketones R^1—CO—CH_2—CO—R^2 and their copper(II) complexes

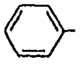
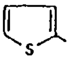
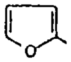
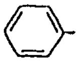
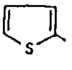
	R^1	R^2	Abbreviation	Complex
HL^1	$^tC_4H_9$	$^tC_4H_9$	Hdpm	$[Cu(dpm)_2]$
	$^iC_3H_7$	$^iC_3H_7$	Hdibm	$[Cu(dibm)_2]$
HL^2	$^nC_3H_7$	$^nC_3H_7$	Hdnbm	$[Cu(dnbm)_2]$
	C_2H_5	C_2H_5	Hdprm	$[Cu(dprm)_2]$
	CH_3	CH_3	Hacac	$[Cu(acac)_2]$
HL^3		CH_3	Hbzac	$[Cu(bzac)_2]$
		CH_3	Htac	$[Cu(tac)_2]$
		CH_3	Hfac	$[Cu(fac)_2]$
		CF_3	Htfbzac	$[Cu(tfbzac)_2]$
		CF_3	Htftac	$[Cu(tftac)_2]$
		CF_3	Htffac	$[Cu(tffac)_2]$

Table 2. Diffuse reflectance, IR spectral and microanalytical data for the complexes of $[Cu(L^1)_2]$ and $[Cu(L^2)_2]$ with 1H-pyrazoles

	Complex	Diffuse reflectance spectra λ_{max} (nm)	IR spectra Assignment (cm^{-1})		Analysis (%)[a]		
			ν(C—O)	ν(C=C)	C	H	N
1t	$[Cu_4(\mu_4\text{-}O)(dpm)_4(\mu\text{-}pz)_2]$	550	1568 1555	1539	52.8 (52.8)	6.8 (7.3)	5.3 (4.9)
2t	$[Cu_4(\mu_4\text{-}O)(dibm)_4(\mu\text{-}pz)_2]$	556	1567	1535	49.1 (49.2)	6.4 (6.5)	5.5 (5.5)
3t	$[Cu_4(\mu_4\text{-}O)(dibm)_4(\mu\text{-}4\text{-}mpz)_2]$	578	1588 1575	1536	50.3 (50.2)	6.8 (6.7)	5.3 (5.3)
4s	$[Cu(dibm)(4\text{-}mpz)(4\text{-}Hmpz)]$	589	1587 1577	1533	53.2 (53.4)	6.6 (6.9)	14.3 (14.7)
5d	$[Cu_2(dnbm)_2(\mu\text{-}3\text{-}mpz)_2]$	639	1583	1524	51.8 (52.1)	6.5 (6.7)	8.8 (9.3)
6d	$[Cu_2(dnbm)_2(\mu\text{-}4\text{-}mpz)_2]$	643	1582	1521	51.4 (52.1)	6.2 (6.7)	9.3 (9.3)
7d	$[Cu_2(dnbm)_2(\mu\text{-}3,5\text{-}dmpz)_2]$	637	1584	1525	52.9 (53.6)	6.8 (7.1)	8.8 (8.9)
8d	$[Cu_2(dnbm)_2(\mu\text{-}pz)_2]$	635[b]	1582	1519			
9d	$[Cu_2(dprm)_2(\mu\text{-}pz)_2]$	618[b]	1581	1521			
10d	$[Cu_2(acac)_2(\mu\text{-}pz)_2]$	630[b]	1589	1523			

[a] Required values are given in parentheses.

[b] These values are taken from Ref. 3.

coordination sphere is listed in Table 4. The complex is tetranuclear and four copper atoms have an approximately tetrahedral arrangement. They are linked by an oxygen atom, which has approximately tetrahedral coordination geometry. This tetrahedral arrangement of the copper atoms is commonly observed in tetranuclear complexes.[11] The geometry about a copper atom is approximately square planar with a central oxygen atom, two oxygen atoms from a bidentate dibm ligand and a nitrogen atom from a bidentate 4-mpz ligand.

The Cu—O and Cu—N distances are 1.934(2) and 1.934(5) Å, respectively, and these are equal to the average value of all Cu—X distances (X = O, N), which is 1.934(2) Å.

The complex **1t** has also been prepared by the reaction of $[Cu_4(\mu_3\text{-}OCH_3)_2(\mu\text{-}OCH_3)_2(dpm)_4]$ with 1H-pyrazole and the crystal structure has been determined by X-ray analysis.[12] The basic structure of **1t** is similar to that of **3t** with four tetrahedrally arranged copper atoms of square-planar geometry. An average value [1.930(6) Å] of all Cu—X distances is very similar to that of **3t**.

Formation reactions

The formation reactions of tetranuclear complexes are very sensitive to the nature of the solvent and 1H-pyrazoles, as shown in Scheme 1. Although the reactions of $[Cu(dpm)_2]$ and $[Cu(dibm)_2]$ with 1H-pyrazole yielded **1t** and **2t**, respectively, in ethanol, they gave coordination polymers $[Cu(\mu\text{-}pz)_2 \cdot nH_2O]$[13] ($n = 1/2$ and 1) in light petroleum. Exceptionally, when $[Cu(dibm)_2]$ reacted with 4-methyl-1H-pyrazole in light petroleum, **4s** was obtained. The complex **4s** changed into **3t** by recrystallization from light petroleum. It is probably formed by hydrolysis of four molecules of **4s** with one molecule of water, isolating six molecules of 4-Hmpz. The complex **4s** may be assumed as an isolated intermediate of the reaction leading to **3t**.

Contrary to the $[Cu(L^1)_2]$ complexes, $[Cu(L^2)_2]$ complexes yielded dinuclear complexes in the reaction with 1H-pyrazole. From these results, it is suggested that the bulky groups such as isopropyl and t-butyl interfere with the formation of dinuclear complexes. It is also suggested that methyl group(s) in 3-Hmpz or 3,5-Hdmpz interfere very little with the formation of dinuclear complexes, although they hinder the formation of tetranuclear complexes.

The reactions of $[Cu(L^3)_2]$ with 1H-pyrazole lead to adducts and/or substitution complexes and are affected by the solvent used. All the reaction products of $[Cu(L^3)_2]$ with 1H-pyrazole were obtained in cyclohexane, except for 1 : 1 adducts [Cu

Table 3. Diffuse reflectance, IR spectral and microanalytical data for the complexes of $[Cu(L^3)_2]$ with 1H-pyrazole

Complex	Diffuse reflectance spectra λ_{max} (nm)	IR spectra ν(N—H)(cm^{-1})	Analysis (%)[a] C	H	N
Coordination polymer					
11p $[\{Cu(tac)(\mu\text{-}pz)\}_n]$	552		38.0	1.9	7.9
			(37.6)	(2.0)	(8.0)
12p $[\{Cu(fac)(\mu\text{-}pz)\}_n]$	558		40.1	1.9	8.4
			(39.3)	(2.1)	(8.3)
13p $[\{Cu(tfbzac)(\mu\text{-}pz)\}_n]$	567		44.6	3.4	9.1
			(44.4)	(3.4)	(9.4)
14p $[\{Cu(tftac)(\mu\text{-}pz)\}_n]$	564		46.7	3.7	9.9
			(46.9)	(3.6)	(9.9)
15p $[\{Cu(tffac)(\mu\text{-}pz)\}_n]$	566		46.0	2.4	8.2
			(45.2)	(2.6)	(8.1)
1 : 1 Adduct					
16a $[Cu(tfbzac)_2(Hpz)]$	>750	3408	49.1	2.7	5.0
			(49.2)	(2.9)	(5.0)
17a $[Cu(tftac)_2(Hpz)]$	>750	3406	39.5	1.8	4.8
			(39.8)	(2.1)	(4.9)
18a $[Cu(tffac)_2(Hpz)]$	>750	3391	42.1	1.9	5.6
			(42.1)	(2.2)	(5.2)
1 : 2 Adduct					
19b $[Cu(tac)_2(Hpz)_2]$	661	3221	49.8	4.1	10.2
			(49.5)	(4.1)	(10.5)
20b $[Cu(fac)_2(Hpz)_2]$	663	3161	52.7	4.5	11.3
			(52.6)	(4.4)	(11.2)

[a] Required values are given in parentheses.

$(tac)_2(Hpz)]$ and $[Cu(fac)_2(Hpz)]^3$, which were prepared in dichloromethane.

Coordination polymers were obtained by the reaction of $[Cu(L^3)_2]$ with 1H-pyrazole, except for $[Cu(bzac)_2]$, but not with methyl-substituted 1H-pyrazoles. This may be due to the steric hindrance of the methyl group(s).

Although the complex $[Cu(bzac)_2]$ produced no 1 : 2 adduct, the complexes $[Cu(tac)_2]$ and $[Cu(fac)_2]$ gave 1 : 2 adducts **19b** and **20b**, respectively. The stability of these adducts is probably due to the resonance stabilization effects of thienyl and furyl groups on the complexes.[3,14]

Diffuse reflectance spectral study

The diffuse reflectance spectra of the tetranuclear complexes resemble each other, showing broad maxima in the region 550–578 nm. The spectrum of **4s** also resembles that of **3t**, which suggests that the copper atom in **4s** has a square-planar geometry.

The coordination polymers have broad maxima in the region 552–567 nm and are different from those of the dinuclear complexes. Their spectra are rather similar to those of coordination polymers $[\{Cu(L)(\mu\text{-}im)\}_n]^3$ (Him = 1H-imidazole) and the tetranuclear complexes **1t** and **3t**. Thus, the coordination polymer probably consists of four-coordinated copper atoms with a square-planar geometry, as shown in Fig. 2.

The diffuse reflectance spectra of the 1 : 1 adducts **16a**–**18a** are different from those of some N-axial adducts such as $[Cu(bzac)_2(Hpz)]^3$ (λ_{max} = 675 nm), and resemble that of an N-equatorial complex, $[Cu(hfac)_2(5\text{-}Hmpz)]^4$ (793 nm; 5-Hmpz = 5-methyl-1H-pyrazole), showing a broad maximum at >750 nm. It suggests that the coordination environments of these adducts are similar and copper atoms in these complexes have an N-equatorial square-pyramidal geometry.

IR spectral study

For the dinuclear complexes, unsplit C—O and C=C bands were observed in the regions 1589–1581 and 1525–1519 cm^{-1}, respectively. For **4s**, split

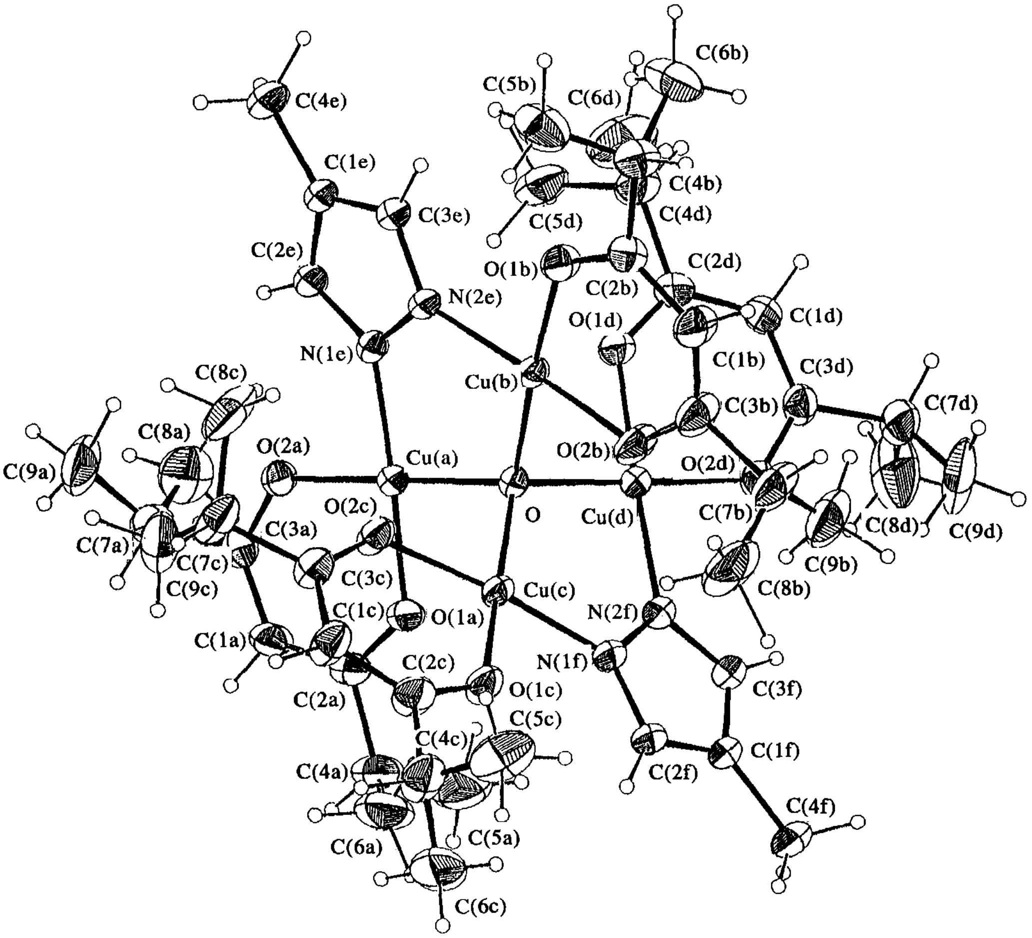


Fig. 1. A perspective drawing of the structure of complex **3t**, showing the numbering scheme (30% probability thermal ellipsoids).

Table 4. Selected bond lengths (Å) and angles (°) for complex **3t**

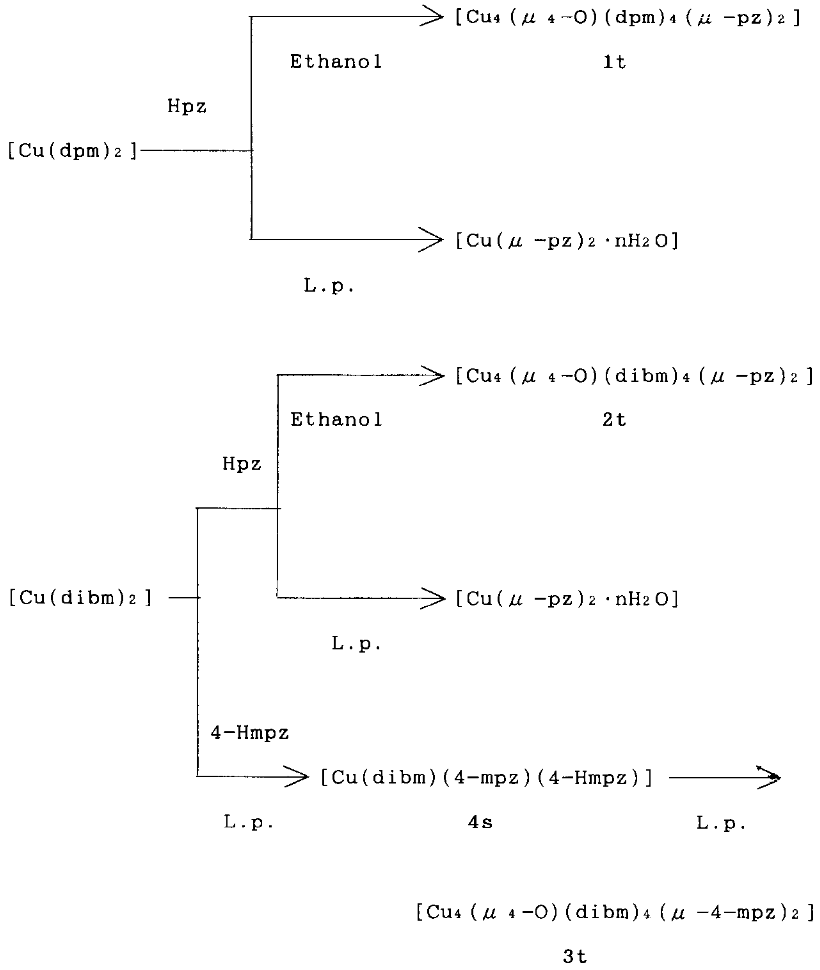
Cu(a)—O	1.936(5)	Cu(b)—O	1.939(5)
Cu(c)—O	1.939(5)	Cu(d)—O	1.941(4)
Cu(a)—O(1a)	1.935(5)	Cu(b)—O(1b)	1.926(5)
Cu(c)—O(1c)	1.930(6)	Cu(d)—O(1d)	1.920(5)
Cu(a)—O(2a)	1.929(5)	Cu(b)—O(2b)	1.925(6)
Cu(c)—O(2c)	1.942(5)	Cu(d)—O(2d)	1.943(5)
Cu(a)—N(1e)	1.929(6)	Cu(b)—N(2e)	1.931(6)
Cu(c)—N(1f)	1.949(6)	Cu(d)—N(2f)	1.928(6)
Cu(d)—O—Cu(a)	122.0(3)	Cu(d)—O—Cu(c)	112.9(2)
Cu(d)—O—Cu(b)	99.5(2)	Cu(a)—O—Cu(c)	100.9(2)
Cu(a)—O—Cu(b)	113.4(2)	Cu(c)—O—Cu(b)	108.0(3)

bands were observed at 1587 and 1577 cm^{-1}, with approximate intensities of 1 : 1, which may arise from non-equivalent C—O bonds in the dibm chelate ring. Similarly split *ν* (C—O) bands, which arise from non-equivalent C—O bonds in the chelated hfac ligand, were observed for $[Zn(hfac)_2(py)_2]$[15], $[Cu(hfac)_2(5\text{-}Hmpz)]$,[4] $[Cu(hfac)_2(mpydz)_2]$ (mpydz = 3-methylpyridazine)[16] and $[\{Cu(hfac)_2\}_3(\mu\text{-}tmpyz)_2]$ (tmpyz = 2,3,5-trimethylpyrazine).[16]

Split bands with approximate intensities of 1 : 1 were also observed for the tetranuclear complexes **1t** and **3t**. These splittings may be due to the non-equivalent dpm or dibm chelate rings in the complex, although all the C—O and C=C bond lengths have average values for both complexes.

The IR spectra of the tetra- and dinuclear complexes have no *ν*(N—H) bands showing that they have no neutral 1H-pyrazole ligands. On the other hand, the IR spectrum of **4s** has a sharp band at 3437 cm^{-1}, which is definitely assignable to a *ν*(N—H) vibration of the free imino group.[4,5] Thus, in **4s** a copper atom is coordinated with a neutral 4-Hmpz, a monodentate 4-mpz and a bidentate dibm ligand.

The *ν*(N—H) bands of the 1 : 1 adducts **16a**–**18a**



Scheme 1. Reaction products of $[Cu(dpm)_2]$ and $[Cu(dibm)_2]$ with 1H-pyrazoles.

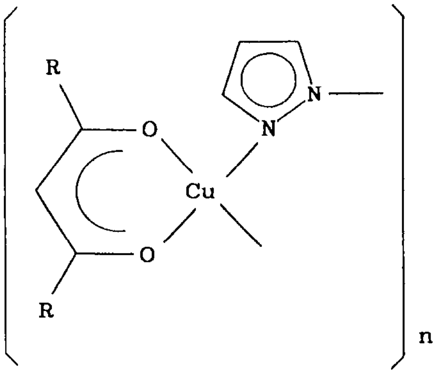


Fig. 2. Proposed structure of the coordination polymer.

were observed in the region 3408–3391 cm^{-1}. These values are slightly lower than that of N-equatorial $[Cu(hfac)_2(5\text{-}Hmpz)]$[4] (3425 cm^{-1}), but considerably higher than those of some other N-axial adducts.[3] Thus, in agreement with the diffuse reflectance data, it is suggested that these adducts have an N-equatorial square-pyramidal structure.

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