sind. Der mittlere Cl—O Abstand und die O—Cl—O Winkel stimmen sehr gut mit jenen anderer Perchlorate überein (Beveridge, Bushnell & Kirk, 1985; Dauter, Hansen, Mawby, Probitts & Reynolds, 1985; Figgis, Wadley & Graham, 1972; Garland, Le Marouille & Spodine, 1985; *International Tables for X-ray Crystallography,* 1968; Thompson, Calabrese & Whitney, 1985). Die Temperaturfaktoren der Perchloratsauerstoffatome sind relativ hoch. Große Beweglichkeiten der Perchlorationen bis zu verschiedenen Disorder-Phänomenen aufgrund der offensichtlich schwachen Wechselwirkung der Perchlorationen mit den umgebenden Molekülen sind auch in anderen Perchloraten zu finden (Dauter *et al.,* 1985; Figgis *et al.,* 1972; Garland *et al.,* 1985). Die Mobilität der ClO_4-Gruppen ist in $[Fe(C_3H_7NS)_6](ClO_4)_2$ wesentlich kleiner als in $[Fe(C_3H_7NO)_6](ClO_4)_2$ (Baumgartner, 1986), möglicherweise aufgrund der größeren Acidität der H-Atome der Methylgruppen in der Nähe der Perchlorationen im DMTF und damit wegen der etwas stärkeren Donor–Akzeptor Wechselwirkung zwischen den Perchloratsauerstoffatomen und den Liganden (kleinster C—H···O Abstand: 3,39 Å).

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Structure of Cu^{II} and Co^{II} Clusters of 7-Azaindolate: $[Cu_2(C_7H_5N_2)_4(dmf)_2]$ (I), $[Cu_4(OCH_3)_4(C_7H_5N_2)_4(dmf)_2]$ (II) and $[Co_4O(C_7H_5N_2)_6].CHCl_3$ (III)

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Abstract. (I) Tetrakis(7-azaindolato)bis(dimethylformamide)dicopper(II), $[Cu_2(C_7H_5N_2)_4(C_3H_7NO)_2]$, $M_r = 741\cdot84$, monoclinic, $P2_1/n$, $a = 9\cdot377$ (6), $b = 13\cdot854$ (3), $c = 12\cdot928$ (4) Å, $\beta = 94\cdot10$ (4)°, $V = 1675\cdot07$ Å^3, $Z = 2$, $D_m = 1\cdot48$, $D_x = 1\cdot47$ Mg m^{-3}, $\mu = 1\cdot318$ mm^{-1}, λ(Mo $K\alpha$) = 0·7093 Å, $F(000) = 764$, final $R = 0\cdot044$ for 1712 observations. (II) Tetrakis(7-azaindolato)bis(dimethylformamide)tetra(methanolato)tetracopper(II), $[Cu_4(C_7H_5N_2)_4(CH_3O)_4(C_3H_7NO)_2]$, $M_r = 993\cdot01$, triclinic, $P\bar{1}$, $a = 9\cdot189$ (3), $b = 9\cdot511$ (2), $c = 12\cdot704$ (2) Å, $\alpha = 88\cdot09$ (2), $\beta = 83\cdot26$ (3), $\gamma = 66\cdot75$ (3)°, $V = 1012\cdot91$ Å^3, $Z = 1$,

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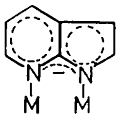
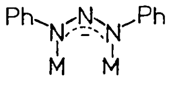
$D_m = 1{\cdot}63$, $D_x = 1{\cdot}63$ Mg m^{-3}, $\mu = 2{\cdot}135$ mm^{-1}, λ(Mo $K\alpha$) = 0·7093 Å, $F(000) = 508$, final $R = 0{\cdot}041$ for 4217 observations. (III) Hexakis(7-azaindolato)oxotetracobalt(II)–trichloromethane (1/1), $[Co_4(C_7H_5N_2)_6O].CHCl_3$, $M_r = 1073{\cdot}90$, triclinic, $P\bar{1}$, $a = 10{\cdot}165\ (3)$, $b = 10{\cdot}389\ (3)$, $c = 20{\cdot}603\ (3)$ Å, $\alpha = 98{\cdot}21\ (2)$, $\beta = 90{\cdot}83\ (2)$, $\gamma = 96{\cdot}04\ (2)°$, $V = 2140{\cdot}71$ Å^3, $Z = 2$, $D_m = 1{\cdot}66$, $D_x = 1{\cdot}67$ Mg m^{-3}, $\mu = 1{\cdot}567$ mm^{-1}, λ(Mo $K\alpha$) = 0·7093 Å, $F(000) = 1080$, final $R = 0{\cdot}062$ for 2846 observations. All three of the title compounds exhibit ligand disorder. In (I), the Cu—Cu distance is 2·782 (2) Å; Cu—O 2·325 Å. In (II) Cu ions occur in square-pyramidal [Cu—N 1·993 (2), Cu—O(methoxide) 1·939 (2), Cu—O(dmf) 2·422 (3) Å] and square-planar [Cu—N 1·966 (2), Cu—O(methoxide) 1·926 Å] coordination geometries. The Cu—Cu distances, 2·999 (1) and 3·014 Å, are long. In (III), the Co—Co distance, 3·156 (1) Å, is also long. The presence of superexchange magnetic interactions is indicated in (II) and (III).

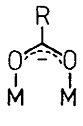
Introduction. Transition-metal complexes with unsaturated electron-rich ligands are of interest, owing to their unusual spectroscopic, magnetic, redox and structural properties (Balch & Holm, 1966; Lauher & Ibers, 1975; Peng & Goedken, 1976; Peng, Liaw, Wang & Simon, 1985; Peng, Chen, Liaw, Chen & Wang, 1985). The anion of 7-azaindole, which is similar to the dpt (1,3-diphenyltriazene) and carboxylate ions, has a potential capacity to coordinate on two metals to form *-M–L–M-* links.



L = 7-azaindolate



1,3-diphenyltriazenate



carboxylate

A series of complexes containing L (Co_4OL_6, Ni_2L_4 and $Cu_2L_4L'_2$ complexes) has been reported (Brookes & Martin, 1974, 1975*a*,*b*). The three title compounds were prepared and their structures were determined in order to study the extent of π-electron delocalization of the 7-azaindolate anion and the metal–metal interaction in the metal clusters.

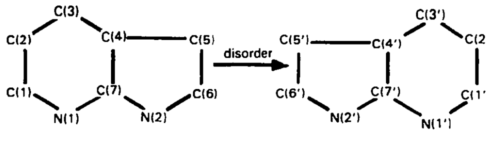
Experimental. Crystals of compounds (I), (II) were obtained by mixing $Cu(OAc)_2$, 7-azaindole and methanolic KOH in dimethylformamide (dmf) solution. X-ray analysis: CAD-4 diffractometer. D_m measured by flotation. Absorption correction according to the experimental φ rotation. For (I): crystal size $0{\cdot}10 \times 0{\cdot}10 \times 0{\cdot}30$ mm, $2\theta_{max} = 50°$, $-11 \le h \le 9$, $0 \le k \le 16$, $0 \le l \le 15$. Unit-cell parameters from 25 reflections ($18 < 2\theta < 25°$). Three standard reflections, 2944 unique reflections measured, 1712 reflections considered observed with $I > 3\sigma(I)$. $R = 0{\cdot}048$, $wR = 0{\cdot}044$, $S = 1{\cdot}93$ based on F. 218 variables refined. $w = 1/[\sigma^2(F_o) + (0{\cdot}01F_o)^2]$. For (II): crystal size $0{\cdot}10 \times 0{\cdot}10 \times 0{\cdot}30$ mm, $2\theta_{max} = 60°$, $-12 \le h \le 12$, $-12 \le k \le 13$, $0 \le l \le 17$. Unit-cell parameters from 25 reflections ($12 < 2\theta < 23°$). Three standard reflections, 5885 unique reflections measured, 4217 reflections considered observed with $I > 2\sigma(I)$. $R = 0{\cdot}041$, $wR = 0{\cdot}035$, $S = 3{\cdot}11$ based on F. 274 variables refined. $w = 1/[\sigma^2(F_o) + (0{\cdot}01F_o)^2]$. Structures were solved by Patterson synthesis. H atoms found on difference Fourier synthesis were fixed by least-squares process. $(\Delta/\sigma)_{max} = 0{\cdot}13$, peak on final difference Fourier map $< 0{\cdot}51$ e Å^{-3} for (I). $(\Delta/\sigma)_{max} = 0{\cdot}01$, peak on final difference Fourier map $< 0{\cdot}62$ e Å^{-3} for (II). Compound (III) was prepared by mixing $Co(OAc)_2$, 7-azaindole and KOH in MeOH solution. Crystal ($0{\cdot}03 \times 0{\cdot}03 \times 0{\cdot}10$ mm) was obtained by dissolving compound (III) in $CHCl_3$ solution followed by slow evaporation. X-ray analysis: CAD-4 diffractometer. D_m measured by flotation. Absorption correction by φ rotation. $2\theta_{max} = 50°$, $-12 \le h \le 12$, $-12 \le k \le 11$, $0 \le l \le 24$. Unit-cell parameters from 25 reflections ($14 < 2\theta < 21°$). Three standard reflections, 7521 unique reflections measured, 2846 reflections considered observed with $I > 2\sigma(I)$. $R = 0{\cdot}062$, $wR = 0{\cdot}0517$, $S = 2{\cdot}04$ based on F. 300 variables refined. $w = 1/[\sigma^2(F_o) + (0{\cdot}01F_o)^2]$. Structure obtained by Patterson synthesis. H atoms found on difference Fourier synthesis were fixed by least-squares process. $(\Delta/\sigma)_{max} = 0{\cdot}02$, peak on final difference Fourier map $< 0{\cdot}66$ e Å^{-3}. Atomic scattering factors calculated by the analytical form using the coefficients in *International Tables for X-ray Crystallography* (1974). Programs from NRCC PDP-11 package (Gabe & Lee, 1981).

Table 1. *Atomic positional parameters and equivalent isotropic temperature factors of* $[Cu_2(C_7H_5N_2)_4(dmf)_2]$

	x	y	z	B_{iso}(Å^2)
Cu	0·38762 (6)	0·05328 (5)	0·03546 (5)	3·74 (2)
N	0·0151 (5)	0·2226 (3)	0·1554 (4)	4·7 (2)
N(1*A*)	0·4941 (4)	−0·0489 (3)	0·8285 (3)	4·6 (2)
N(2*A*)	0·3083 (4)	0·0458 (3)	0·8884 (3)	4·2 (2)
N(1*B*)	0·4956 (5)	0·1726 (3)	−0·0034 (4)	4·2 (2)
N(2*B*)	0·6834 (4)	0·0786 (3)	−0·0622 (4)	4·4 (3)
O	0·2027 (4)	0·1448 (3)	0·0954 (3)	6·3 (3)
C(1)	0·0845 (7)	0·1477 (4)	0·1247 (5)	5·8 (4)
C(2)	0·0780 (8)	0·3146 (5)	0·1527 (6)	8·5 (6)
C(3)	−0·1264 (7)	0·2176 (5)	0·1912 (6)	7·7 (5)
C(1*A*)	0·5347 (7)	−0·0900 (5)	0·7411 (5)	6·0 (4)
C(2*A*)	0·4498 (8)	−0·0787 (5)	0·6506 (6)	7·6 (5)
C(4*A*)	0·2915 (8)	0·0046 (5)	0·7163 (5)	7·6 (6)
C(5*A*)	0·1519 (6)	0·0722 (5)	0·7440 (5)	6·2 (4)
C(6*A*)	0·1853 (6)	0·0877 (4)	0·8488 (5)	5·2 (4)
C(7*A*)	0·3715 (5)	−0·0009 (4)	0·8154 (4)	3·7 (3)
C(1*B*)	0·4486 (6)	0·2623 (4)	0·0046 (5)	5·6 (4)
C(2*B*)	0·5239 (7)	0·3406 (4)	−0·0264 (5)	6·1 (4)
C(3*B*)	0·6535 (6)	0·3308 (4)	−0·0696 (5)	5·9 (4)
C(4*B*)	0·7059 (6)	0·2417 (4)	−0·0783 (5)	5·1 (3)
C(5*B*)	0·8307 (6)	0·1966 (5)	−0·1144 (6)	6·4 (5)
C(6*B*)	0·8098 (6)	0·1002 (4)	−0·1033 (6)	6·5 (5)
C(7*B*)	0·6208 (5)	0·1631 (3)	−0·0448 (4)	3·7 (3)
C(3*A*) (0·76)*	0·3297 (10)	−0·0313 (7)	0·6388 (8)	8·0 (4)
C(3*A'*) (0·27)*	0·1999 (20)	0·0321 (14)	0·6678 (15)	5·7 (7)

* Occupancy factors of disordered atoms.

Discussion. Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1 for (I), Table 2 for (II), Table 3 for (III).* *ORTEP* (Johnson, 1965) drawings and labeling schemes are given in Fig. 1 for (I), Fig. 2 for (II), Fig. 3 for (III). The bond lengths and angles are tabulated in Tables 4, 5, 6 respectively. All three structures suffer ligand disorder. It was found that there were peaks (1–2 e Å^{-3}) remaining between C(4) and C(5) atoms in some of the ligands. They were assigned as C(3′) atoms and the occupancy factors of C(3) and C(3′) atoms were refined.



Another indication of the disorder of the ligands is the temperature factors of the atoms. N(1), N(2) and C(7) atoms have $B_{\rm iso}$ values around 3 to 4 Å^2 and the remaining atoms of the ligand have higher $B_{\rm iso}$ values (5–8 Å^2).

The first, dimeric, structure, (I), which is similar to that of [$Cu_2(OAc)_4(H_2O)_2$], contains four 7-azaindolate bridges with two Cu ions and two coordinated dmf molecules with Cu—Cu distance 2·782 (2) Å, Cu—N bond length 2·003 (4) Å, Cu—O 2·325 (4) Å. The Cu—Cu distance is longer than those of [$Cu_2(dpt)_4$] (2·40 Å), [$Cu_2(OAc)_4(H_2O)$] (2·64 Å), and shorter than those of [$Cu(ap)_2(H_2O)_4$] (2·95 Å),

Table 2. *Atomic positional parameters and equivalent isotropic temperature factors of* [$Cu_4(C_7H_5N_2)_4$-$(OCH_3)_4(dmf)_2$]

	x	y	z	$B_{\rm iso}$(Å^2)
Cu(1)	0·39871 (5)	0·07936 (5)	0·17520 (4)	2·93 (2)
Cu(2)	0·29301 (5)	0·03420 (5)	−0·03234 (4)	2·95 (2)
O(1)	0·3387 (3)	−0·0622 (3)	0·1024 (2)	3·6 (1)
O(2)	0·3039 (3)	0·1900 (2)	0·0542 (2)	3·5 (1)
O(3)	0·1629 (3)	0·1755 (3)	0·3027 (3)	5·5 (2)
N	−0·0541 (4)	0·1381 (4)	0·3762 (3)	4·2 (2)
N(1A)	0·5275 (3)	0·7632 (3)	0·7841 (2)	3·1 (1)
N(2A)	0·2844 (3)	0·8552 (3)	0·9001 (2)	3·5 (2)
N(1B)	0·5297 (3)	0·9273 (3)	0·2739 (2)	3·2 (1)
N(2B)	0·7702 (3)	0·8350 (3)	0·1559 (2)	3·3 (1)
C(1)	0·0715 (5)	0·1115 (5)	0·3064 (3)	4·3 (2)
C(2)	−0·1023 (6)	0·2578 (5)	0·4539 (4)	6·1 (3)
C(3)	−0·1579 (5)	0·0581 (5)	0·3727 (4)	5·7 (3)
C(4)	0·3625 (5)	−0·2129 (4)	0·1329 (4)	5·1 (3)
C(5)	0·2592 (5)	0·3468 (4)	0·0350 (4)	5·0 (3)
C(1A)	0·6100 (4)	0·6515 (4)	0·7121 (3)	3·6 (2)
C(2A)	0·5501 (6)	0·5460 (5)	0·6900 (4)	5·6 (3)
C(3A) (0·76)*	0·5781 (7)	0·4631 (6)	0·2705 (5)	5·8 (4)
C(4A)	0·3442 (6)	0·6410 (4)	0·7958 (4)	6·0 (3)
C(5A)	0·1659 (5)	0·6879 (5)	0·8698 (4)	5·7 (3)
C(6A)	0·1580 (5)	0·8140 (4)	0·9228 (3)	4·2 (2)
C(7A)	0·3902 (4)	0·7565 (4)	0·8278 (3)	3·0 (2)
C(1B)	0·4747 (5)	0·9072 (5)	0·3723 (3)	4·1 (2)
C(2B)	0·5714 (6)	0·8036 (5)	0·4380 (4)	5·7 (3)
C(3B) (0·79)*	0·7141 (7)	0·7186 (6)	0·4180 (4)	5·0 (3)
C(4B)	0·7699 (5)	0·7361 (4)	0·3250 (3)	5·0 (3)
C(5B)	0·9500 (5)	0·6572 (5)	0·2548 (4)	5·5 (3)
C(6B)	0·9220 (5)	0·7306 (4)	0·1613 (3)	4·0 (2)
C(7B)	0·6844 (4)	0·8378 (4)	0·2492 (3)	2·9 (2)
C(3A′) (0·33)*	0·7500 (15)	0·4056 (14)	0·1908 (11)	4·6 (4)
C(3B′) (0·34)*	0·8917 (14)	0·6467 (14)	0·3340 (10)	4·6 (4)

* Occupancy factors of disordered atoms.

Table 3. *Positional and thermal parameters of* [Co_4-$(C_7H_5N_2)_6O$].$CHCl_3$

	x	y	z	$B_{\rm iso}$(Å^2)
Co(1)	0·1489 (2)	0·2413 (2)	0·1856 (1)	3·2 (1)
Co(2)	0·9093 (2)	0·3634 (2)	0·2584 (1)	3·5 (1)
Co(3)	0·0369 (2)	0·1272 (2)	0·3126 (1)	3·3 (1)
Co(4)	0·1926 (2)	0·4082 (2)	0·3275 (1)	3·8 (1)
O	0·0735 (8)	0·2844 (8)	0·2713 (4)	2·9 (2)
N(1A)	0·0961 (12)	0·5212 (12)	0·3929 (6)	4·4 (3)
N(2A)	−0·1071 (11)	0·5085 (12)	0·3311 (6)	3·9 (3)
C(1A)	0·1545 (17)	0·5791 (17)	0·4498 (9)	5·8 (4)
C(2A)	0·0936 (19)	0·6709 (19)	0·4922 (10)	7·1 (5)
C(3A) (0·8)*	−0·0162 (23)	0·7016 (23)	0·4815 (12)	6·7 (6)
C(4A)	−0·0828 (17)	0·6525 (17)	0·4305 (9)	5·6 (4)
C(5A)	−0·2209 (18)	0·6553 (18)	0·3970 (9)	6·2 (5)
C(6A)	−0·2217 (16)	0·5695 (17)	0·3411 (8)	5·3 (4)
C(7A)	−0·0253 (15)	0·5578 (15)	0·3845 (8)	4·3 (4)
N(1B)	0·3154 (11)	0·3206 (11)	0·3795 (6)	4·0 (3)
N(2B)	0·1737 (11)	0·1245 (11)	0·3839 (6)	3·8 (3)
C(1B)	0·4342 (16)	0·3834 (16)	0·4026 (8)	5·0 (4)
C(2B)	0·5140 (19)	0·3355 (19)	0·4430 (10)	7·4 (5)
C(3B)	0·4762 (20)	0·2257 (20)	0·4642 (10)	8·1 (6)
C(4B)	0·3662 (16)	0·1503 (16)	0·4460 (8)	4·7 (4)
C(5B)	0·2962 (17)	0·0290 (18)	0·4547 (9)	6·2 (5)
C(6B)	0·1804 (16)	0·0131 (16)	0·4160 (8)	5·2 (4)
C(7B)	0·2823 (14)	0·2058 (14)	0·4005 (7)	3·3 (3)
N(1C)	0·0197 (11)	0·2483 (11)	0·1118 (6)	3·7 (3)
N(2C)	−0·0948 (12)	0·4158 (12)	0·1692 (6)	4·2 (3)
C(1C)	0·0420 (16)	0·1913 (16)	0·0516 (8)	4·8 (4)
C(2C)	−0·0141 (17)	0·2307 (18)	−0·0007 (9)	6·1 (5)
C(3C) (0·8)*	−0·0785 (22)	0·3297 (21)	0·0000 (11)	5·8 (6)
C(4C)	−0·1057 (18)	0·3891 (17)	0·0545 (9)	6·1 (5)
C(5C)	−0·1835 (17)	0·5003 (17)	0·0837 (9)	5·9 (5)
C(6C)	−0·1709 (16)	0·5089 (16)	0·1500 (8)	5·4 (4)
C(7C)	−0·0579 (14)	0·3459 (14)	0·1133 (7)	3·6 (3)
N(1D)	0·0643 (11)	0·9676 (11)	0·2496 (6)	3·5 (3)
N(2D)	0·2046 (11)	1·0623 (11)	0·1749 (6)	3·5 (3)
C(1D)	0·0176 (15)	0·8517 (15)	0·2662 (8)	4·5 (4)
C(2D)	0·0579 (18)	0·7352 (18)	0·2365 (9)	6·1 (5)
C(3D)	0·1420 (18)	0·7313 (18)	0·1873 (9)	6·3 (5)
C(4D)	0·1935 (15)	0·8381 (15)	0·1676 (8)	4·2 (4)
C(5D)	0·2833 (16)	0·8798 (16)	0·1201 (8)	4·8 (4)
C(6D)	0·2859 (15)	1·0119 (15)	0·1259 (7)	4·0 (4)
C(7D)	0·1489 (14)	0·9599 (14)	0·2008 (7)	3·2 (3)
N(1E)	0·7524 (11)	0·2341 (11)	0·2663 (6)	3·6 (3)
N(2E)	0·8527 (12)	0·1120 (12)	0·3417 (6)	4·4 (3)
C(1E)	0·6362 (15)	0·2464 (16)	0·2354 (8)	4·7 (4)
C(2E)	0·5189 (16)	0·1774 (16)	0·2492 (8)	5·1 (4)
C(3E)	0·5182 (16)	0·0891 (16)	0·2911 (8)	5·4 (4)
C(4E)	0·6282 (16)	0·0696 (16)	0·3234 (8)	4·6 (4)
C(5E)	0·6674 (16)	−0·0071 (16)	0·3700 (8)	5·1 (4)
C(6E)	0·7997 (15)	0·0227 (15)	0·3792 (8)	4·5 (4)
C(7E)	0·7454 (14)	0·1441 (14)	0·3071 (7)	3·6 (3)
N(1F)	0·3069 (12)	0·5206 (12)	0·2758 (6)	4·6 (3)
N(2F)	0·2952 (12)	0·3788 (12)	0·1730 (6)	4·7 (3)
C(1F)	0·3713 (19)	0·6383 (19)	0·3049 (10)	7·1 (5)
C(2F)	0·4639 (22)	0·7011 (22)	0·2702 (11)	9·1 (6)
C(3F) (0·8)*	0·4893 (30)	0·6642 (30)	0·2165 (16)	11·0 (10)
C(4F)	0·4433 (18)	0·5648 (18)	0·1823 (9)	6·7 (5)
C(5F)	0·4465 (22)	0·4832 (22)	0·1088 (11)	9·5 (7)
C(6F)	0·3515 (19)	0·3765 (19)	0·1126 (9)	7·0 (5)
C(7F)	0·3440 (14)	0·4866 (14)	0·2151 (7)	3·5 (3)
C(3A′) (0·2)*	0·8370 (73)	0·6944 (73)	0·4395 (37)	3·9 (17)
C(3C′) (0·2)*	0·8381 (80)	0·4457 (81)	0·0274 (41)	5·1 (21)
C(3F′) (0·2)*	0·4929 (56)	0·5732 (56)	0·1350 (28)	1·5 (12)
C	0·6572 (19)	0·9540 (19)	0·1031 (10)	7·1 (5)
Cl(1)	0·6804 (7)	1·0956 (7)	0·0713 (4)	11·6 (6)
Cl(2)	0·6150 (6)	0·8242 (6)	0·0456 (3)	9·0 (4)
Cl(3)	0·7856 (6)	0·9348 (8)	0·1535 (3)	11·1 (6)

* Occupancy factor of disordered atoms

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* Lists of anisotropic thermal parameters, structure factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43230 (114 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$[Cu_2(ad)_4(H_2O)_2]$ (2·95 Å), $[Cu_2(OAc)_4(p\text{-tol})_2]$ (3·2 Å) (Table 7). The direct magnetic interaction of this complex is comparable to those in Table 7.

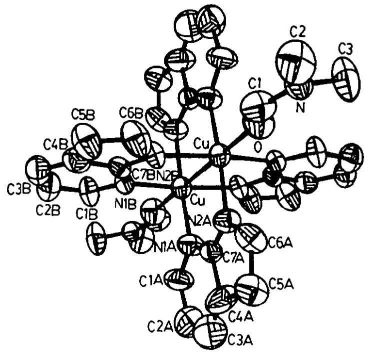

Fig. 1. *ORTEP* (Johnson, 1965) plot of the $[Cu_2(C_7H_5N_2)_4(dmf)_2]$ molecule with labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

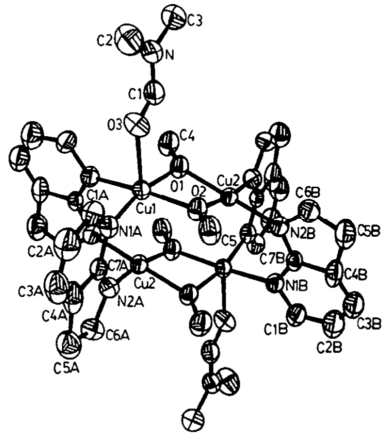

Fig. 2. *ORTEP* plot of the $[Cu_4(C_7H_5N_2)_4(OCH_3)_4(dmf)_2]$ molecule with labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

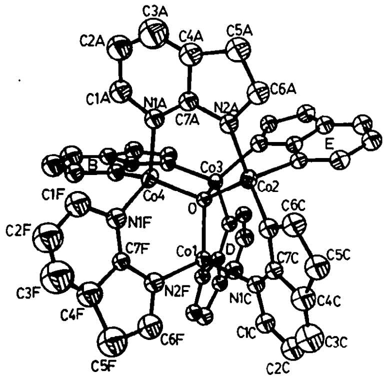

Fig. 3. *ORTEP* plot of the $[Co_4(C_7H_5N_2)_6O]$ molecule with labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 4. *Bond lengths* (Å) *and bond angles* (°) *for* $[Cu(C_7H_5N_2)_4(dmf)_2]$

Cu–Cu	2·782 (1)	N(2B)–C(7B)	1·335 (6)
Cu–N(1B)	2·021 (4)	C(2A)–C(3A)	1·30 (1)
N–C(1)	1·303 (7)	C(4A)–C(3A)	1·20 (1)
N(1A)–C(1A)	1·345 (7)	C(5A)–C(3A')	1·24 (2)
N(2A)–C(7A)	1·319 (6)	C(3B)–C(4B)	1·337 (8)
N(2B)–C(6B)	1·367 (7)	C(5B)–C(6B)	1·359 (8)
C(1A)–C(2A)	1·377 (9)	Cu–N(2A)	1·994 (4)
C(4A)–C(7A)	1·439 (8)	Cu–O	2·325 (3)
C(5A)–C(6A)	1·384 (9)	N–C(3)	1·438 (7)
C(2B)–C(3B)	1·380 (8)	N(2A)–C(6A)	1·358 (6)
C(4B)–C(7B)	1·435 (7)	N(1B)–C(7B)	1·331 (6)
Cu–N(1A)	2·012 (4)	O–C(1)	1·197 (7)
Cu–N(2B)	1·984 (4)	C(4A)–C(5A)	1·67 (1)
N–C(2)	1·405 (8)	C(4A)–C(3A')	1·09 (2)
N(1A)–C(7A)	1·328 (6)	C(1B)–C(2B)	1·369 (8)
N(1B)–C(1B)	1·325 (6)	C(4B)–C(5B)	1·433 (8)

Cu–Cu–N(1A)	83·6 (1)	Cu–Cu–N(2A)	84·1 (1)
Cu–Cu–N(1B)	87·0 (1)	Cu–Cu–N(2B)	80·8 (1)
Cu–Cu–O	178·9 (1)	N(1A)–Cu–N(2A)	167·6 (1)
N(1A)–Cu–N(1B)	89·3 (1)	N(1A)–Cu–N(2B)	89·5 (1)
N(1A)–Cu–O	95·9 (1)	N(2A)–Cu–N(1B)	88·0 (1)
N(2A)–Cu–N(2B)	90·7 (1)	N(2A)–Cu–O	96·3 (1)
N(1B)–Cu–N(2B)	167·8 (1)	N(1B)–Cu–O	92·0 (1)
N(2B)–Cu–O	100·2 (1)	C(1)–N–C(2)	119·7 (5)
C(1)–N–C(3)	123·5 (5)	C(2)–N–C(3)	116·8 (5)
Cu–N(1A)–C(1A)	123·4 (3)	Cu–N(1A)–C(7A)	123·0 (3)
C(1A)–N(1A)–C(7A)	113·6 (4)	Cu–N(2A)–C(6A)	125·9 (3)
Cu–N(2A)–C(7A)	123·4 (3)	C(6A)–N(2A)–C(7A)	110·7 (4)
Cu–N(1B)–C(1B)	125·0 (3)	Cu–N(1B)–C(7B)	119·4 (3)
C(1B)–N(1B)–C(7B)	115·6 (4)	Cu–N(2B)–C(6B)	125·5 (3)
Cu–N(2B)–C(7B)	128·4 (3)	C(6B)–N(2B)–C(7B)	106·1 (4)
Cu–O–C(1)	148·5 (4)	N–C(1)–O	128·1 (5)
N(1A)–C(1A)–C(2A)	119·0 (5)	C(1A)–C(2A)–C(3A)	126·8 (7)
C(5A)–C(4A)–C(7A)	101·9 (4)	C(5A)–C(4A)–C(3A)	134·4 (7)
C(5A)–C(4A)–C(3A')	48· (1)	C(7A)–C(4A)–C(3A)	123·7 (8)
C(7A)–C(4A)–C(3A')	150· (1)	C(3A)–C(4A)–C(3A')	86· (1)
C(4A)–C(5A)–C(6A)	99·9 (4)	C(4A)–C(5A)–C(3A')	41·0 (9)
C(6A)–C(5A)–C(3A')	141· (1)	N(2A)–C(6A)–C(5A)	115·4 (5)
N(1A)–C(7A)–N(2A)	125·7 (4)	N(1A)–C(7A)–C(4A)	122·1 (5)
N(2A)–C(7A)–C(4A)	112·2 (4)	N(1B)–C(1B)–C(2B)	122·6 (5)
C(1B)–C(2B)–C(3B)	121·9 (5)	C(2B)–C(3B)–C(4B)	117·7 (5)
C(3B)–C(4B)–C(5B)	138·0 (5)	C(3B)–C(4B)–C(7B)	117·4 (5)
C(5B)–C(4B)–V(7B)	104·6 (4)	C(4B)–C(5B)–C(6B)	105·5 (4)
N(2B)–C(6B)–C(5B)	113·1 (5)	N(1B)–C(7B)–N(2B)	124·4 (4)
N(1B)–C(7B)–C(4B)	124·9 (4)	N(2B)–C(7B)–C(4B)	110·7 (4)
C(2A)–C(3A)–C(4A)	114·8 (9)	C(4A)–C(3A')–C(5A)	91· (1)

Table 5. *Bond lengths* (Å) *and angles* (°) *for* $[Cu_4(OCH_3)_2(C_7H_5N_2)_4(dmf)_2]$

Cu(1)–Cu(2)	3·0141 (8)	N(1B)–C(7B)	1·342 (4)
Cu(1)–O(2)	1·927 (2)	C(1A)–C(2A)	1·371 (5)
Cu(1)–N(1B)	1·993 (2)	C(4A)–C(5A)	1·691 (7)
Cu(2)–N(2A)	1·965 (2)	C(5A)–C(6A)	1·368 (5)
O(2)–C(5)	1·403 (4)	C(2B)–C(3B)	1·239 (7)
N–C(2)	1·428 (5)	C(4B)–C(7B)	1·413 (4)
N(1A)–C(7A)	1·342 (4)	C(5B)–C(3B')	1·10 (1)
N(1B)–C(1B)	1·330 (4)	Cu(1)–O(1)	1·939 (2)
N(2B)–C(7B)	1·339 (4)	Cu(1)–N(1A)	1·976 (2)
C(3A)–C(4A)	1·248 (7)	Cu(2)–O(2)	1·915 (2)
C(4A)–C(3A')	1·11 (1)	O(1)–C(4)	1·410 (4)
C(1B)–C(2B)	1·373 (5)	N–C(1)	1·315 (5)
C(4B)–C(5B)	1·678 (6)	N(1A)–C(1A)	1·344 (4)
C(5B)–C(6B)	1·357 (6)	N(2A)–C(7A)	1·340 (4)
Cu(1)–Cu(2)	2·999 (1)	N(2B)–C(6B)	1·363 (4)
Cu(1)–O(3)	2·422 (3)	C(2A)–C(3A)	1·260 (7)
Cu(2)–O(1)	1·926 (2)	C(4A)–C(7A)	1·410 (4)
Cu(2)–N(2B)	1·966 (2)	C(5A)–C(3A')	1·16 (1)
O(3)–C(1)	1·212 (4)	C(3B)–C(4B)	1·264 (7)
N–C(3)	1·440 (5)	C(4B)–C(3B')	1·12 (1)
N(2A)–C(6A)	1·363 (4)		

Cu(2)–Cu(1)–Cu(2)	77·97 (3)	Cu(2)–Cu(1)–O(1)	38·59 (7)
Cu(2)–Cu(1)–O(2)	38·18 (6)	Cu(2)–Cu(1)–O(3)	107·22 (7)
Cu(2)–Cu(1)–N(1A)	129·18 (8)	Cu(2)–Cu(1)–N(1B)	130·61 (8)
Cu(2)–Cu(1)–O(1)	87·78 (8)	Cu(2)–Cu(1)–O(2)	86·02 (8)
Cu(2)–Cu(1)–O(3)	174·76 (7)	Cu(2)–Cu(1)–N(1A)	83·52 (9)
Cu(2)–Cu(1)–N(1B)	82·60 (9)	O(1)–Cu(1)–O(2)	75·30 (9)

Table 5 (*cont.*)

O(1)–Cu(1)–O(3)	96·8 (1)	O(1)–Cu(1)–N(1A)	166·8 (1)
O(1)–Cu(1)–N(1B)	96·3 (1)	O(2)–Cu(1)–O(3)	97·6 (1)
O(2)–Cu(1)–N(1A)	94·2 (1)	O(2)–Cu(1)–N(1B)	166·1 (1)
O(3)–Cu(1)–N(1A)	92·4 (1)	O(3)–Cu(1)–N(1B)	94·3 (1)
N(1A)–Cu(1)–N(1B)	92·4 (1)	Cu(1)–Cu(2)–Cu(1)	102·03 (3)
Cu(1)–Cu(2)–O(1)	38·92 (6)	Cu(1)–Cu(2)–O(2)	38·46 (7)
Cu(1)–Cu(2)–N(2A)	132·78 (9)	Cu(1)–Cu(2)–N(2B)	133·30 (8)
Cu(1)–Cu(2)–O(1)	106·69 (8)	Cu(1)–Cu(2)–O(2)	104·96 (8)
Cu(1)–Cu(2)–N(2A)	78·57 (9)	Cu(1)–Cu(2)–N(2B)	79·42 (9)
O(1)–Cu(2)–O(2)	75·88 (9)	O(1)–Cu(2)–N(2A)	94·9 (1)
O(1)–Cu(2)–N(2B)	170·3 (1)	O(2)–Cu(2)–N(2A)	170·7 (1)
O(2)–Cu(2)–N(2B)	95·4 (1)	N(2A)–Cu(2)–N(2B)	93·6 (1)
Cu(1)–O(1)–Cu(2)	102·5 (1)	Cu(1)–O(1)–C(4)	126·4 (2)
Cu(2)–O(1)–C(4)	129·4 (2)	Cu(1)–O(2)–Cu(2)	103·4 (1)
Cu(1)–O(2)–C(5)	127·2 (2)	Cu(2)–O(2)–C(5)	129·4 (2)
Cu(1)–O(3)–C(1)	117·4 (2)	C(1)–N–C(2)	121·3 (3)
C(1)–N–C(3)	122·0 (3)	C(2)–N–C(3)	116·5 (3)
Cu(1)–N(1A)–C(1A)	123·8 (2)	Cu(1)–N(1A)–C(7A)	122·7 (2)
C(1A)–N(1A)–C(7A)	113·5 (2)	Cu(2)–N(2A)–C(6A)	121·8 (2)
Cu(2)–N(2A)–C(7A)	129·5 (2)	C(6A)–N(2A)–C(7A)	108·7 (2)
Cu(1)–N(1B)–C(1B)	123·6 (2)	Cu(1)–N(1B)–C(7B)	123·6 (2)
C(1B)–N(1B)–C(7B)	112·8 (2)	Cu(2)–N(2B)–C(6B)	122·7 (2)
Cu(2)–N(2B)–C(7B)	128·8 (2)	C(6B)–N(2B)–C(7B)	108·3 (3)
O(3)–C(1)–N	126·1 (3)	N(1A)–C(1A)–C(2A)	119·6 (3)
C(1A)–C(2A)–C(3A)	128·3 (4)	C(2A)–C(3A)–C(4A)	112·3 (4)
C(3A)–C(4A)–C(5A)	133·0 (4)	C(3A)–C(4A)–C(7A)	126·1 (4)
C(3A)–C(4A)–C(3A′)	90·1 (7)	C(5A)–C(4A)–C(7A)	100·8 (3)
C(5A)–C(4A)–C(3A′)	43·0 (7)	C(7A)–C(4A)–C(3A′)	143·8 (8)
C(4A)–C(5A)–C(6A)	100·2 (3)	C(4A)–C(5A)–C(3A′)	40·9 (6)
C(6A)–C(5A)–C(3A′)	141·0 (7)	N(2A)–C(6A)–C(5A)	116·1 (3)
N(1A)–C(7A)–N(2A)	125·7 (2)	N(1A)–C(7A)–C(4A)	120·1 (3)
N(2A)–C(7A)–C(4A)	114·2 (3)	N(1B)–C(1B)–C(2B)	121·2 (3)
C(1B)–C(2B)–C(3B)	127·9 (4)	C(2B)–C(3B)–C(4B)	112·2 (4)
C(3B)–C(4B)–C(5B)	134·1 (3)	C(3B)–C(4B)–C(7B)	125·9 (4)
C(3B)–C(4B)–C(3B′)	93·4 (7)	C(5B)–C(4B)–C(7B)	100·0 (3)
C(5B)–C(4B)–C(3B′)	40·7 (6)	C(7B)–C(4B)–C(3B′)	140·6 (7)
C(4B)–C(5B)–C(6B)	101·3 (3)	C(4B)–C(5B)–C(3B′)	41·5 (6)
C(6B)–C(5B)–C(3B′)	142·8 (7)	N(2B)–C(6B)–C(5B)	115·8 (3)
N(1B)–C(7B)–N(2B)	125·4 (3)	N(1B)–C(7B)–C(4B)	119·9 (3)
N(2B)–C(7B)–C(4B)	114·6 (3)	C(4A)–C(3A′)–C(5A)	96·1 (9)

Table 6. *Bond lengths* (Å) *and angles* (°) *for* $[Co_4(C_7H_5N_2)_6O].CHCl_3$

Co(1)–O	1·917 (8)	C(2C)–C(3C)	1·28 (2)
Co(1)–N(2F)	2·00 (1)	C(4C)–C(7C)	1·42 (2)
Co(2)–N(2C)	1·96 (1)	C(5C)–C(3C′)	1·23 (8)
Co(3)–N(2B)	1·99 (1)	N(2D)–C(6D)	1·38 (1)
Co(4)–O	1·905 (8)	C(2D)–C(3D)	1·32 (2)
Co(4)–N(1F)	1·98 (1)	C(4D)–C(7D)	1·46 (2)
N(2A)–C(6A)	1·39 (2)	N(1E)–C(7E)	1·33 (1)
C(2A)–C(3A)	1·22 (2)	C(1E)–C(2E)	1·38 (2)
C(4A)–C(7A)	1·43 (2)	C(4E)–C(5E)	1·40 (2)
C(5A)–C(3A′)	1·04 (7)	N(1F)–C(1F)	1·37 (2)
N(2B)–C(6B)	1·41 (2)	N(2F)–C(7F)	1·35 (1)
C(2B)–C(3B)	1·30 (2)	C(3F)–C(4F)	1·20 (3)
C(4B)–C(7B)	1·46 (2)	C(4F)–C(3F′)	1·10 (6)
N(1C)–C(7C)	1·35 (1)	C–Cl(1)	1·68 (2)
C(1C)–C(2C)	1·33 (2)	Co(1)–N(2D)	1·98 (1)
C(4C)–C(5C)	1·52 (2)	Co(2)–N(2A)	1·97 (1)
C(5C)–C(6C)	1·33 (2)	Co(3)–O	1·942 (8)
N(1D)–C(7D)	1·32 (1)	Co(3)–N(2E)	1·97 (1)
C(1D)–C(2D)	1·38 (2)	Co(4)–N(1B)	1·99 (1)
C(4D)–C(5D)	1·42 (2)	N(1A)–C(7A)	1·34 (1)
N(1E)–C(1E)	1·35 (1)	C(1A)–C(2A)	1·39 (2)
N(2E)–C(7E)	1·38 (1)	C(4A)–C(5A)	1·56 (2)
C(3E)–C(4E)	1·34 (2)	C(5A)–C(6A)	1·33 (2)
C(5E)–C(6E)	1·35 (2)	N(1B)–C(7B)	1·33 (1)
N(2F)–C(6F)	1·35 (2)	C(1B)–C(2B)	1·32 (2)
C(2F)–C(3F)	1·14 (3)	C(4B)–C(5B)	1·42 (2)
C(4F)–C(7F)	1·46 (2)	N(1C)–C(1C)	1·31 (1)
C(5F)–C(3F′)	1·07 (6)	N(2C)–C(7C)	1·33 (1)
C–Cl(3)	1·69 (1)	C(3C)–C(4C)	1·23 (2)
Co(1)–N(1C)	1·99 (1)	C(4C)–C(3C′)	1·06 (8)
Co(2)–O	1·965 (8)	N(1D)–C(1D)	1·34 (1)
Co(2)–N(1E)	2·00 (1)	N(2D)–C(7D)	1·33 (1)
Co(3)–N(1D)	1·99 (1)	C(3D)–C(4D)	1·29 (2)
Co(4)–N(1A)	1·98 (1)	C(5D)–C(6D)	1·36 (2)

Table 6 (*cont.*)

N(1A)–C(1A)	1·32 (2)	N(2E)–C(6E)	1·35 (2)
N(2A)–C(7A)	1·36 (1)	C(2E)–C(3E)	1·33 (2)
C(3A)–C(4A)	1·24 (2)	C(4E)–C(7E)	1·42 (2)
C(4A)–C(3A′)	0·97 (7)	N(1F)–C(7F)	1·30 (1)
N(1B)–C(1B)	1·35 (1)	C(1F)–C(2F)	1·35 (3)
N(2B)–C(7B)	1·33 (1)	C(4F)–C(5F)	1·60 (2)
C(3B)–C(4B)	1·31 (2)	C(5F)–C(6F)	1·40 (2)
C(5B)–C(6B)	1·39 (2)	C–Cl(2)	1·66 (1)
N(2C)–C(6C)	1·39 (2)		

O–Co(1)–N(1C)	111·3 (4)	O–Co(1)–N(2D)	111·0 (4)
O–Co(1)–N(2F)	109·4 (4)	N(1C)–Co(1)–N(2D)	107·8 (4)
N(1C)–Co(1)–N(2F)	103·8 (5)	N(2D)–Co(1)–N(2F)	113·3 (4)
O–Co(2)–N(2A)	110·1 (4)	O–Co(2)–N(2C)	109·3 (4)
O–Co(2)–N(1E)	110·1 (4)	N(2A)–Co(2)–N(2C)	113·4 (4)
N(2A)–Co(2)–N(1E)	104·9 (4)	N(2C)–Co(2)–N(1E)	108·9 (4)
O–Co(3)–N(2B)	109·6 (4)	O–Co(3)–N(1D)	111·5 (4)
O–Co(3)–N(2E)	109·9 (4)	N(2B)–Co(3)–N(1D)	101·6 (4)
N(2B)–Co(3)–N(2E)	115·3 (4)	N(1D)–Co(3)–N(2E)	108·7 (4)
O–Co(4)–N(1A)	111·2 (4)	O–Co(4)–N(1B)	111·6 (4)
O–Co(4)–N(1F)	112·1 (4)	N(1A)–Co(4)–N(1B)	107·2 (4)
N(1A)–Co(4)–N(1F)	108·7 (5)	N(1B)–Co(4)–N(1F)	105·7 (5)
Co(1)–O–Co(2)	108·5 (4)	Co(1)–O–Co(3)	109·7 (4)
Co(1)–O–Co(4)	110·1 (4)	Co(2)–O–Co(3)	110·4 (4)
Co(2)–O–Co(4)	108·6 (4)	Co(3)–O–Co(4)	109·6 (4)
Co(4)–N(1A)–C(1A)	121· (1)	Co(4)–N(1A)–C(7A)	127· (1)
C(1A)–N(1A)–C(7A)	112· (1)	Co(2)–N(2A)–C(6A)	123·1 (9)
Co(2)–N(2A)–C(7A)	130·5 (9)	C(6A)–N(2A)–C(7A)	106· (1)
N(1A)–C(1A)–C(2A)	121· (1)	C(1A)–C(2A)–C(3A)	124· (1)
C(2A)–C(3A)–C(4A)	122· (2)	C(3A)–C(4A)–C(5A)	140· (1)
C(3A)–C(4A)–C(7A)	117· (1)	C(3A)–C(4A)–C(3A′)	99· (4)
C(5A)–C(4A)–C(7A)	102· (1)	C(5A)–C(4A)–C(3A′)	41· (4)
C(7A)–C(4A)–C(3A′)	143· (4)	C(4A)–C(5A)–C(6A)	104· (1)
C(4A)–C(5A)–C(3A′)	38· (4)	C(6A)–C(5A)–C(3A′)	142· (4)
N(2A)–C(6A)–C(5A)	115· (1)	N(1A)–C(7A)–N(2A)	123· (1)
N(1A)–C(7A)–C(4A)	124· (1)	N(2A)–C(7A)–C(4A)	113· (1)
Co(4)–N(1B)–C(1B)	121· (1)	Co(4)–N(1B)–C(7B)	123·5 (9)
C(1B)–N(1B)–C(7B)	115· (1)	Co(3)–N(2B)–C(6B)	121·2 (9)
Co(3)–N(2B)–C(7B)	129·2 (9)	C(6B)–N(2B)–C(7B)	108· (1)
N(1B)–C(1B)–C(2B)	123· (1)	C(1B)–C(2B)–C(3B)	119· (1)
C(2B)–C(3B)–C(4B)	126· (1)	C(3B)–C(4B)–C(5B)	142· (1)
C(3B)–C(4B)–C(7B)	113· (1)	C(5B)–C(4B)–C(7B)	105· (1)
C(4B)–C(5B)–C(6B)	108· (1)	N(2B)–C(6B)–C(5B)	109· (1)
N(1B)–C(7B)–N(2B)	127· (1)	N(1B)–C(7B)–C(4B)	123· (1)
N(2B)–C(7B)–C(4B)	110· (1)	Co(1)–N(1C)–C(1C)	119·0 (9)
Co(1)–N(1C)–C(7C)	121·8 (9)	C(1C)–N(1C)–C(7C)	114· (1)
Co(2)–N(2C)–C(6C)	125· (1)	Co(2)–N(2C)–C(7C)	125·4 (9)
C(6C)–N(2C)–C(7C)	107· (1)	N(1C)–C(1C)–C(2C)	119· (1)
C(1C)–C(2C)–C(3C)	127· (1)	C(2C)–C(3C)–C(4C)	119· (2)
C(3C)–C(4C)–C(5C)	140· (1)	C(3C)–C(4C)–C(7C)	118· (1)
C(3C)–C(4C)–C(3C′)	87· (4)	C(5C)–C(4C)–C(7C)	102· (1)
C(5C)–C(4C)–C(3C′)	53· (4)	C(7C)–C(4C)–C(3C′)	155· (4)
C(4C)–C(5C)–C(6C)	106· (1)	C(4C)–C(5C)–C(3C′)	44· (3)
C(6C)–C(5C)–C(3C′)	150· (4)	N(2C)–C(6C)–C(5C)	112· (1)
N(1C)–C(7C)–N(2C)	124· (1)	N(1C)–C(7C)–C(4C)	123· (1)
N(2C)–C(7C)–C(4C)	113· (1)	Co(3)–N(1D)–C(1D)	117·9 (9)
Co(3)–N(1D)–C(7D)	126·3 (9)	C(1D)–N(1D)–C(7D)	114· (1)
Co(1)–N(2D)–C(6D)	125·3 (9)	Co(1)–N(2D)–C(7D)	127·2 (9)
C(6D)–N(2D)–C(7D)	106· (1)	N(1D)–C(1D)–C(2D)	123· (1)
C(1D)–C(2D)–C(3D)	121· (1)	C(2D)–C(3D)–C(4D)	121· (1)
C(3D)–C(4D)–C(5D)	140· (1)	C(3D)–C(4D)–C(7D)	116· (1)
C(5D)–C(4D)–C(7D)	104· (1)	C(4D)–C(5D)–C(6D)	107· (1)
N(2D)–C(6D)–C(5D)	113· (1)	N(1D)–C(7D)–N(2D)	124· (1)
N(1D)–C(7D)–C(4D)	125· (1)	N(2D)–C(7D)–C(4D)	111· (1)
Co(2)–N(1E)–C(1E)	119·5 (9)	Co(2)–N(1E)–C(7E)	125·3 (9)
C(1E)–N(1E)–C(7E)	115· (1)	Co(3)–N(2E)–C(6E)	125·0 (9)
Co(3)–N(2E)–C(7E)	125·3 (9)	C(6E)–N(2E)–C(7E)	104· (1)
N(1E)–C(1E)–C(2E)	122· (1)	C(1E)–C(2E)–C(3E)	120· (1)
C(2E)–C(3E)–C(4E)	122· (1)	C(3E)–C(4E)–C(5E)	139· (1)
C(3E)–C(4E)–C(7E)	115· (1)	C(5E)–C(4E)–C(7E)	106· (1)
C(4E)–C(5E)–C(6E)	106· (1)	N(2E)–C(6E)–C(5E)	114· (1)
N(1E)–C(7E)–N(2E)	124· (1)	N(1E)–C(7E)–C(4E)	126· (1)
N(2E)–C(7E)–C(4E)	110· (1)	Co(4)–N(1F)–C(1F)	122· (1)
Co(4)–N(1F)–C(7F)	125· (1)	C(1F)–N(1F)–C(7F)	112· (1)
Co(1)–N(2F)–C(6F)	119· (1)	Co(1)–N(2F)–C(7F)	130· (1)
C(6F)–N(2F)–C(7F)	111· (1)	N(1F)–C(1F)–C(2F)	119· (1)
C(1F)–C(2F)–C(3F)	124· (2)	C(2F)–C(3F)–C(4F)	127· (3)
C(3F)–C(4F)–C(5F)	143· (2)	C(3F)–C(4F)–C(7F)	114· (2)
C(3F)–C(4F)–C(3F′)	101· (3)	C(5F)–C(4F)–C(7F)	103· (1)
C(5F)–C(4F)–C(3F′)	41· (3)	C(7F)–C(4F)–C(3F′)	144· (3)
C(4F)–C(5F)–C(6F)	102· (1)	C(4F)–C(5F)–C(3F′)	43· (3)
C(6F)–C(5F)–C(3F′)	145· (3)	N(2F)–C(6F)–C(5F)	114· (1)
N(1F)–C(7F)–N(2F)	126· (1)	N(1F)–C(7F)–C(4F)	123· (1)
N(2F)–C(7F)–C(4F)	110· (1)	C(4A)–C(3A′)–C(5A)	101· (6)
C(4C)–C(3C′)–C(5C)	83· (5)	C(4F)–C(3F′)–C(5F)	96· (4)
Cl(1)–C–Cl(2)	114· (1)	Cl(1)–C–Cl(3)	112· (1)

Table 7. *Comparison of the structure and magnetic interaction of dinuclear copper complexes*

	Structure type	Cu—Cu distance	Magnetism BM*	Magnetism $2J$(cm^{-1})	Reference
$[Cu(dpt)_2]_2$	dimer	2·44 Å	diamagnetism		Harris, Hoskins & Martin (1959); Martin & Waterman (1959)
$[Cu(C_5H_4NO)_2(dmso)]_2$	dimer	2·588			Peng, Liaw & Yeh (1986)
$[Cu(DMB)(OAc)(H_2O)]_2$	dimer	2·597		−325	Erre, Micera, Piu, Cariati & Ciani (1985)
$[Cu(DMB^a)_2(H_2O)]_2$	dimer	2·620		−250	Erre, Micera, Piu, Cariati & Ciani (1985)
$[Cu(2\text{-}BrC_6H_4COO)(H_2O)]_2$	dimer	2·624			Harrison, Rettig & Trotter (1972)
$[Cu(OAc)_2(H_2O)]_2$	dimer	2·64	1·39	−286	Van Niekerk & Schoening (1953); Figgis & Martin (1956)
$[Cu(OAc)_2py]_2$	dimer	2·64		−325	Kokot & Martin (1964); Barclay & Kennard (1961); Hanic. Stempelova & Hanicova (1964)
$[Cu(CH_3CONHCOO)(H_2O)]_2$	dimer	2·666	1·4		Udupa & Krebs (1979)
$[Cu(C_7H_5N_2)_2(dmf)]_2$	dimer	2·782	1·27		Present work
$[Cu(adH^b)_2(H_2O)_2]_2(ClO_4)_4$	dimer	2·95	1·45		Terzis, Beauchamp & Rivest (1973)
$[Cu(ad^c)_2(H_2O)_2]_2$	dimer	2·95		−257	Goodgame & Price (1968); Sletten (1967, 1969)
$[Cu(ap^d)_2(H_2O)_4]_2$	dimer	2·95		−185	Weiss & Venner (1963); Asakawa, Inoue, Hara & Kubo (1972)
$[CuCl_2(hpH^e)_2(H_2O)]_2$	dimer	3·024	1·38	−200	Weiss & Venner (1963); Asakawa, Inoue, Hara & Kubo (1972)
$[CuCl(apH^f)_2\frac{3}{2}(H_2O)]_2$	dimer	3·066	1·39	−206	Weiss & Venner (1963); Asakawa, Inoue, Hara & Kubo (1972)
$[Cu_2(ade^b)_4Cl_2]Cl_2.6H_2O$	dimer	3·066	1·45		de Meester & Skapski (1971)
$[Cu(OAc)_2.p\text{-}tol]_2$	chain	3·2		−105	Yawney, Moreland & Doedens (1973)

Notes: *a* DMB = 2,6-methoxybenzoato, *b* adH = adenine = ade, *c* ad = adeninato, *d* ap = 6-aminopurinato, *e* apH = 6-aminopurine, *f* hpH = 6-hydroxypurine.

* 1 BM ≡ $9{\cdot}27 \times 10^{-24}$ JT^{-1}.

The second, tetrameric, structure, (II), contains four methoxide bridges, four 7-azaindolate bridges and two coordinated dmf molecules. Two kinds of Cu ions were found in the structure; one has square pyramidal coordination geometry with Cu(1)—N 1·993 (2) Å, Cu(1)—O (methoxide) 1·939 (2) Å, Cu(1)—O (dmf) 2·422 (3) Å, the other has square planar geometry with Cu(2)—N 1·966 (2) Å, Cu(2)—O (methoxide) 1·926 (2) Å. The geometry and long Cu(1)—Cu(2) distances, 2·999 (1) and 3·014 (1) Å, of this complex indicate the presence of a superexchange magnetic interaction.

The third, tetrameric, structure, (III), contains six 7-azaindolate bridges, four tetrahedral Co ions, and an O ion. The central O atom is tetrahedrally surrounded by the four Co atoms and each Co is tetrahedrally coordinated by one O and three N atoms of 7-azaindolate. The structure is similar to those of $[Be_4O(OOCR)_6]$ and $[Zn_4O(OOCR)_6]$ but is the first structure of this type observed for a cobalt complex. The average Co—Co distance, 3·156 (1) Å, is long and indicates the superexchange interaction of this cluster.

In the ligand moiety, the C—N and C—C bond lengths of azaindolate are between those of single-bond and double-bond values. The three structures suffer ligand disorder. It is not possible to estimate quantitatively the extent of π-electron delocalization in the 7-azaindolate ligand.

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Structure of Acetato(benzenethiolato)mercury(II)

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Abstract. $[Hg(C_2H_3O_2)(C_6H_5S)]$, $M_r = 368{\cdot}80$, monoclinic, $P2_1/n$, $a = 18{\cdot}362\ (2)$, $b = 7{\cdot}485\ (1)$, $c = 14{\cdot}292\ (2)$ Å, $\beta = 104{\cdot}72\ (1)°$, $V = 1900{\cdot}0\ (3)$ Å^3, $Z = 8$, $D_x = 2{\cdot}58$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 164$ cm^{-1}, $F(000) = 1344$, $T = 295$ K, $R = 0{\cdot}034$ for 2326 unique observed reflections. The structure is built up of infinite —S—Hg—S— chains linked *via* acetate groups into sheets. The two independent Hg atoms, five- and six-coordinated, are in addition to the two thiolate groups also bonded to two and three acetate ligands, respectively.

Introduction. It has been known for a long time that Hg^{II} forms extremely stable, water insoluble compounds with organic sulfur ligands of the thioalcohol *R*SH (*R* = alkyl, aryl) type. Solid complexes between these thiols and Hg^{II} have been isolated with thiol/mercury (Th/Hg) ratios varying from 1 to 4. Many of these complexes have been the subject of intense spectroscopic investigations and the crystal structures of some of them have been determined. For Th/Hg ratios 3 or 4, thiophenols have mostly been used as ligands, *e.g.* by Christou, Folting & Huffman (1984) and Choudhury, Dance, Guerney & Rae (1983). For structure determinations of the neutral compounds $Hg(SR)_2$ and for the 1:1 complexes $Hg(SR)X$, however, alkyl thiols have so far been preferred as ligands, *e.g.* by Wells (1937), Bradley & Kunchur (1963, 1964), Kunchur (1964), Taylor & Carty (1977), Perchard, Zuppiroli, Gouzerh, Jeannin & Robert (1981), Perchard, Baron & De Loze (1984), Barrera *et al.* (1982), Biscarini, Foresti & Pradella (1984), Canty, Raston & White (1978, 1979*a*,*b*), Johansson (1939) and Puff, Sievers & Elsner (1975). The crystal structures of the 1:1 complexes so far studied (Canty, Raston & White, 1979*a*) have been found to be dependent on the donicity of the anion *X*; the chloride, bromide and acetate anions have been used earlier. In this study acetate and thiophenolate anions were chosen to allow a direct comparison with the previous work.

Experimental. Crystals grown from an acetonitrile solution of mercury acetate and mercury thiophenolate. Plate-shaped transparent crystal, $0{\cdot}25 \times 0{\cdot}20 \times 0{\cdot}09$ mm, CAD-4 diffractometer, graphite-monochromatized Mo *Kα* radiation, variable speed, ω–2θ scans, width $(0{\cdot}80 + 0{\cdot}60\tan\theta)°$, max. recording time 150 s. Three standard reflections, no significant variations. Lattice parameters based on 40 diffractometer θ values. 3585 reflections, $\theta \le 25°$, $0 \le h \le 17$, $0 \le k \le 7$, $-13 \le l \le 13$, 2327 with $I > 3\sigma(I)$. Lp and absorption corrections, transmission factors 0·06–0·22. Structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980). Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$, $w = [\sigma^2(F_o) + (0{\cdot}030F_o)^2 + 2{\cdot}5]^{-1}$, anisotropic temperature factors for non-C atoms and phenyl-H atoms included with fixed parameters in calculated positions [d(C—H) = 1·00 Å]. Final refinement with 2326 reflections, 138 variables, $R = 0{\cdot}034$, $wR = 0{\cdot}041$, $S = 1{\cdot}0$. Corrections for secondary extinction (Zachariasen, 1967), $g = 0{\cdot}19\ (2) \times 10^{-4}$. $(\Delta/\sigma)_{\max} = 0{\cdot}02$, final $\Delta\rho$ excursions $\le |1{\cdot}3|$ e Å^{-3}. Scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Program used: see Lundgren (1982).

Discussion. Final atomic coordinates and temperature factors are listed in Table 1† and selected interatomic distances and angles in Table 2. The present structure may be described as built up of endless $(\text{—Hg—S}R\text{—})_n$ chains running in the *y* direction, linked *via* the acetate

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† Lists of structure factors, anisotropic thermal parameters and phenyl-H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43226 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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