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THE CRYSTAL STRUCTURE OF BINUCLEAR METAL COMPLEXES OF 7-AZAINDOLE: $Cu_2(CH_3CO_2)_2(C_7H_5N_2)_2(C_7H_6N_2)_2$ AND $Ni_2(C_7H_5N_2)_4.2DMF$

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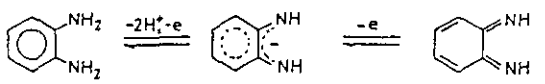
The crystal and molecular structures have been determined by single-crystal X-ray methods for the binuclear metal ions (II) complexes of 7-azaindole (1H-pyrrolo [2,3-b] pyridine, $C_7H_6N_2$ denoted by HL), $Cu_2(CH_3CO_2)_2L_2(HL)_2$ and $Ni_2L_4.2DMF$. The dark green crystal of $Cu_2(CH_3CO_2)_2L_2(HL)_2$ was found to crystallize in the monoclinic space group P $2_1/n$ with a = 9.566(2), b = 12.752(2), c = 12.852(4) Å, β = 99.23(3)^0, V = 1547 Å, Z = 2, the final R = 0.062 and Rw = 0.053 for 1488 observations from 2722 unique reflections. The Cu-Cu distance is 2.747(2), Cu-N (L$^-$, bridge) is 1.966(7), Cu-N (HL, axial) is 2.229(8), and Cu-O is 2.031(6)Å. The red crystal of $Ni_2L_4.2DMF$ was was found to crystallize in the triclinic space group P $\bar{1}$ with a = 8.907(5), b = 9.462(2), c = 10.217(2) Å, α = 90.48(2), β = 91.09(3), γ = 110.69(3)^0, V = 805 Å^3, Z = 1, the final R = 0.063 and Rw = 0.069 for 1489 observations from 2834 unique reflections. The Ni-Ni distance is 2.594(2), Ni-N is 1.905(7) Å. These two molecules lie on crystllographic inversion centers and exhibit ligand disorder.

INTRODUCTION

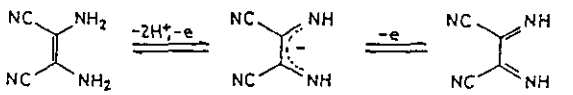
Transition metal complexes with the delocalized, unsaturated, electron-rich ligands such as s-bqdi (1), s-disn (2) etc.[1-4], are of considerable interest owing to their unusual properities[5-7].

The anion of 7-azaindole[8-12] (3), which is similar to the dpt[13-14] (1,3-diphenyltriazene) (4) and carboxylate ions[15-17] (5) of the nonlinear triatomic bidentate groups, has a bridging potential to act as a binuclearing ligand for a number of the transition metals.



o-phenylene-diamine pda | Semi-o-benzoquinone-diimine s-bqdi | o-benzoquinone-diimine bqdi

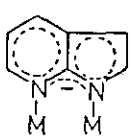
(1)



diaminomaleo-nitrile damn | semi-diimino-succinonitrile s-disn | diiminosuccino-nitrile disn

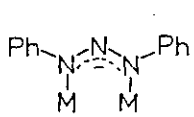
(2)

A series of metal complexes with 7-azaindole have been reported by Brookes and Martin[8-10]. These metal (II) complexes, which contain 7-azaindole coordinated either as the neutral molecule or in the deprotonated form, were characterized through the pysical measurements of magnetic, mass, IR, electronic, and ESR spectroscopy. From these measurements, the molecular structures of these metal compounds were proposed. The proposed



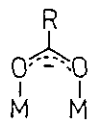
L=7-azaindolate

(3)



1,3-diphenyltriazenate

(4)



carboxylate

(5)

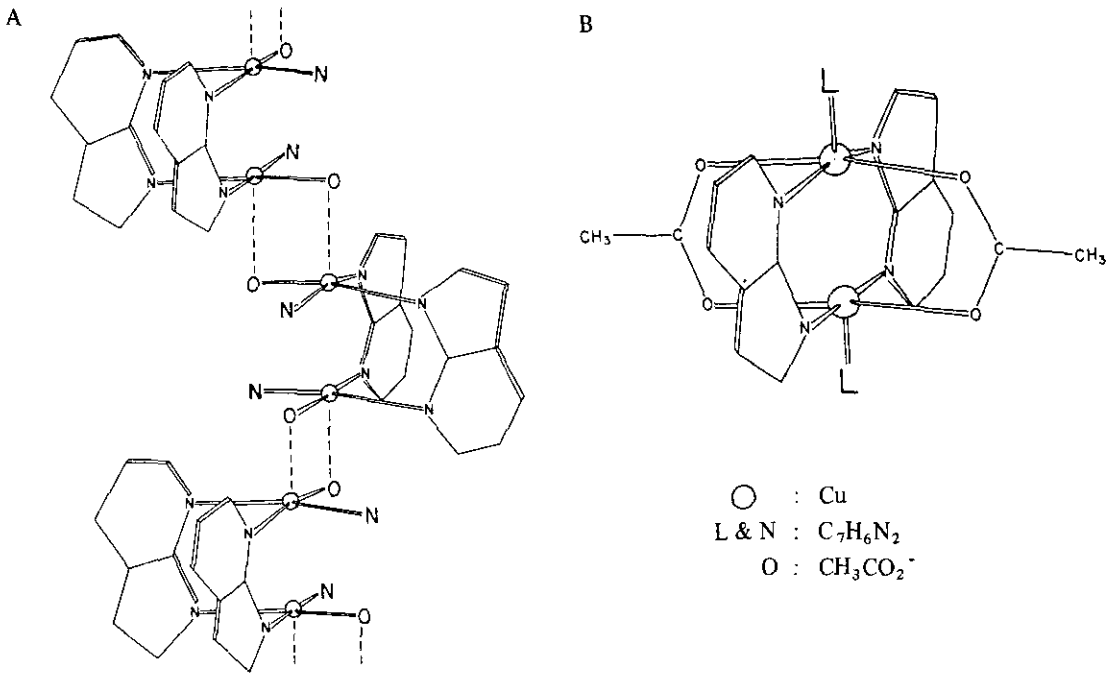


Fig. 1 Alternative molecular structures for $Cu(CH_3CO_2L(HL)$
(A) chain; (B) binuclear.

molecular structures for $[Cu(CH_3CO_2)L(HL)]$ (6) and $[NiL_2]$ (7) are shown in Figure 1, Figure 2.

We have already reported[12] the crystal structure of a dimeric copper·(II) complex, $Cu_2(C_7H_5N_2)_4(dmf)_2$ (8); a tetrameric copper (II) complex, $Cu_4(OCH_3)_4(C_7H_5N_2)_4(dmf)_2$ (9); and a tetrameric cobalt (II) complex, $Co_4O(C_7H_5N_2)_6.CHCl_3$ (10). In this paper the crystal structures of $Cu_2(CH_3CO_2)_2L_2(HL)_2$ and $Ni_2L_4.2DMF$ are described. These structure were determined to study the extent of electron delocalization of the 7-azaindolate anion and metal-metal interaction in the metal clusters.

EXPERIMENT

(1) $Cu_2(CH_3CO_2)_2L_2(HL)_2$, (6)

A solution of copper acetate monohydrate (0.6 g in 40 ml methanol), and a solution of 7-azaindole (0.7 g in 10 ml methanol) were mixed, stirred for 10 mins., then filtered and dried. The green complex of $Cu_2(CH_3CO_2)_2L_2(HL)_2$ was obtained. The single crystal of $Cu_2(CH_3CO_2)_2L_2(HL)_2$ was grown by slow diffusion of the copper complex solution ($CHCl_3$) into the dmf solvent.

Infrared spectra:

The 3323 cm^{-1} peak was assigned to an N-H stretching band which is sharper than the N-H band of the free 7-azaindole. The 669 cm^{-1} peak was

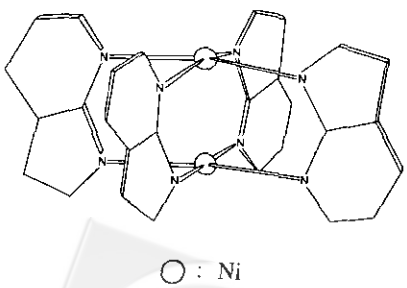


Fig. 2 Proposed molecular structure for NiL_2

assigned to the characteristic OCO deformation. The three strong characteristic absorptions of 7-azaindole are at 804, 765, 738cm^{-1}.

Elemental analysis:

$Cu_2(CH_3CO_2)_2(C_7H_5N_2)_2(C_7H_6N_2)_2$

	C	H	N
found	52.82	3.82	15.45
calc.	53.70	3.94	15.66

(2) Ni_2L_4.2DMF, (7)

The nickel complex, Ni_2L_4, was prepared by the Brookes' method[9]. A solution of nickel acetate tetrahydrate (1.24 g in 100 ml methanol) and a solution of 7-azaindole (1.18 g in 10 ml methanol) were mixed and heated to dryness. The green solid so obtained was dissolved in toluene, then the solution was reheated to dryness (red-green), redissolved in toluene, then refluxed for 1 hr., filtered and dried. The red compound of nickel complex was obtained. The single crystal of Ni_2L_4.2DMF was grown by the slow diffusion of the Ni_2L_4 solution (acetone) into the dmf solvent.

Infrared spectra:

The strong absorption at 1661 cm^{-1} was assigned to the C=0 stretching of dmf. The three strong characteristic absorptions of 7-azaindole are at 790, 755, 718 cm^{-1}.

Elemental analysis:

$Ni_2(C_7H_5N_2)_4$

found	57.09	3.23	18.89
calc.	57.39	3.41	19.10

(3) X-ray analysis

The refined cell constants and other crystal parameters for the copper and nickel complexes are recorded in Table 1, together with details of the intensity measurements. The intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer.

Atomic scattering factors are calculated by the analytical form using the coefficient in International Table IV for X-ray Crystallography (1974), program from NRCC PDP-11 package[18]. Absorption correction is according to the experiment Ψ rotation. Structures were solved by Patterson. Hydrogen atoms found on Difference-Fourrier synthesis were fixed by the least-square process.

DESCRIPTION OF STRUCTURE

The molecular geometries of the binuclearing metal (II) complexes are shown in Figure 3 for $Cu_2(CH_3CO_2)_2L_2(HL)_2$, Figure 4 for Ni_2L_4.2DMF. Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 2 for the copper complex, and Table 3 for the nickel complex. The bond lengths and angles are listed in Tables 4–7. The binuclear structure of $Cu_2(CH_3CO_2)_2L_2(HL)_2$, which is similar to that of $Cu_2(CH_3CO_2)_4(H_2O)_2$, contains two 7-azaindolate and carboxylate bridges with two Cu (II) ion in syn-syn configuration and two monocoordinated HL molecules The Cu-Cu distance is 2.747(2); Cu-N (L^-, bridge), 1.966(7); Cu-N (HL, axial), 2.229(8) and Cu-O, 2.031(6) Å. The dimeric structure of Ni_2L_4. 2DMF contains four bridging 7-azaindolate and two

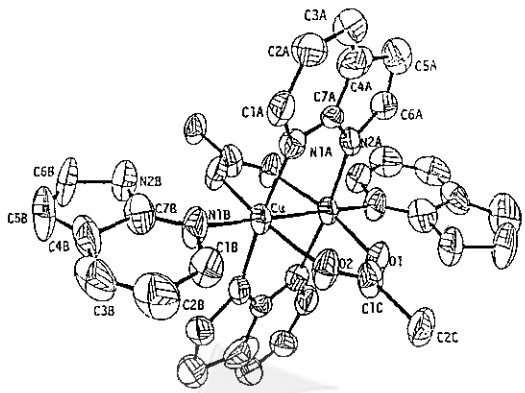


Fig. 3 Molecular structure of $Cu_2(CH_3CO_2)_2(C_7H_5N_2)_2(C_7H_6N_2)_2$

Table 1 Crystallographic parameters

Formula	$Cu_2(CH_3CO_2)_2(C_7H_5N_2)_2(C_7H_6N_2)_2$	$Ni_2(C_7H_5N_2)_4.2DMF$
Molecular Weight	715.71	732.13
Color	dark green	red
Crystal system	monoclinic	triclinic
Space group	$P\,2_1/n$	$P\,\bar{1}$
a, Å	9.566(2)	8.907(5)
b, Å	12.752(2)	9.462(2)
c, Å	12.852(4)	10.217(2)
α , deg		90.48(2)
β , deg	99.23(3)	91.09(3)
γ , deg		110.69(3)
V, Å^3	1547	805
Z	2	1
F(000)	732	412
D_{calcd}, g/cm^3	1.536	1.510
Radiation λ , A	Mo K_α, 0.7093	Mo K_α, 0.7093
Linear abs. coeff., cm^{-1}	14.27	12.30
Scan parameter	2 (0.8 + 0.35tane)	2 (1.2 + 0.35 tane)
Scan speed, deg/min	20/3 – 20/20	20/2 – 20/9
hkl range h:	0–11	0–10
k:	0–15	–11–11
l:	–15–15	–12–12
Reflection collected	2722	2834
Reflection of obs.	1488	1489
No. of variable	217	206
2 θ limit, deg	50	50
Max. of c/s	0.55	0.2
Max. peak of DF-MAP, e$^-$/A^3	0.74	0.79
R	0.062	0.063
Rw	0.053	0.069

Table 2 Atomic positions and thermal parameters of $Cu_2(CH_3CO_2)_2(C_7H_6N_2)_2(C_7H_5N_2)_2$

ATOM	X	Y	Z	BISO
Cu	0.4145(1)	0.0786(1)	0.0271(1)	3.3(1)
N2A	0.5188(9)	0.0570(6)	0.1704(6)	3.2(4)
N1A	0.3339(8)	0.0799(7)	−0.1234(6)	3.2(4)
C6A	0.5040(12)	0.1078(8)	0.2605(8)	3.8(6)
C5A	0.5834(13)	0.0793(10)	0.3522(9)	5.0(7)
C4A	0.6807(15)	−0.0157(12)	0.3006(10)	6.9(10)
C3A	0.7638(20)	−0.0661(15)	0.3449(15)	4.5(11)
C3A'	0.6881(31)	0.0059(22)	0.3821(20)	3.9(16)
C2A	0.1884(13)	0.1383(10)	−0.2774(9)	5.0(8)
C1A	0.2341(11)	0.1455(9)	−0.1712(9)	4.1(6)
C7A	0.6232(11)	−0.0146(8)	0.1953(7)	2.9(5)
N2B	0.1049(10)	0.0846(8)	0.1232(8)	3.9(6)
N1B	0.2741(10)	0.2037(7)	0.0738(8)	4.9(6)
C6B	0.0003(13)	0.0959(12)	0.1923(11)	7.5(10)
C5B	−0.0014(16)	0.1941(12)	0.2271(12)	8.3(11)
C4B	0.0993(14)	0.2552(10)	0.1855(9)	5.5(8)
C3B	0.1544(15)	0.3543(10)	0.1893(10)	6.2(9)
C2B	0.2633(15)	0.3826(9)	0.1367(10)	6.2(9)
C1B	0.3224(12)	0.3052(8)	0.0800(10)	4.6(7)
C7B	0.1683(13)	0.1815(9)	0.1232(10)	5.1(7)
01	0.2917(8)	−0.0498(5)	0.0432(6)	4.6(5)
02	0.5698(8)	0.1764(5)	−0.0011(6)	4.7(5)
C1C	0.3211(12)	−0.1440(8)	0.0286(9)	4.1(7)
C2C	0.2054(12)	−0.2249(9)	0.0415(9)	4.8(7)
H6A	0.4244(0)	0.1702(0)	0.2637(0)	6.3(0)
H5A	0.5921(0)	0.1061(0)	0.4364(0)	6.3(0)
H3A	0.1592(0)	0.1068(0)	−0.4013(0)	6.3(0)
H2A	0.1358(0)	0.1486(0)	−0.3566(0)	6.3(0)
H1A	0.1892(0)	0.2065(0)	−0.1235(0)	6.3(0)
HN2B	0.1471(0)	0.0697(0)	0.1827(0)	6.3(0)
H6B	−0.0723(0)	0.0325(0)	0.2114(0)	6.3(0)
H5B	−0.0629(0)	0.2213(0)	0.2870(0)	6.3(0)
H3B	0.1107(0)	0.4121(0)	0.2374(0)	6.3(0)
H2B	0.2961(0)	0.4651(0)	0.1388(0)	6.3(0)
H1B	0.4122(0)	0.3288(0)	0.0412(0)	6.3(0)
H2CA	0.1711(0)	−0.2432(0)	-0.0375(0)	6.3(0)
H2CB	0.1165(0)	−0.1967(0)	0.0776(0)	6.3(0)
H2CC	0.2451(0)	−0.2963(0)	0.0844(0)	6.3(0)

OCCUPANCY OF C3A = 0.6, OCCUPANCY OF C3A' = 0.4

Table 3 Atomic positions and thermal parameters of $Ni_2(C_7H_5N_2)_4.2DMF$

ATOM	X	Y	Z	BISO
Ni	0.0361(2)	0.1179(1)	0.0766(1)	3.3(1)
N1A	0.2177(9)	0.0758(8)	0.1419(7)	3.6(4)
N2A	−0.1525(9)	0.1399(8)	0.0012(7)	3.9(4)
C1A	0.3234(12)	0.1622(11)	0.2339(9)	4.2(6)
C2A	0.4526(13)	0.1154(12)	0.2715(10)	5.4(7)
C3A	0.4756(13)	−0.0009(14)	0.2206(12)	6.4(8)
C4A	0.3744(12)	−0.0869(12)	0.1298(10)	4.6(6)
C5A	−0.3538(14)	0.2267(13)	−0.0474(12)	6.1(7)
C6A	−0.2173(12)	0.2460(11)	0.0259(10)	4.8(6)
C7A	0.2430(11)	−0.0442(10)	0.0889(9)	3.7(5)
N1B	−0.0888(9)	−0.0122(9)	0.2066(7)	4.0(4)
N2B	0.1622(9)	0.2278(8)	−0.0612(7)	3.7(4)
C1B	−0.1122(12)	0.0255(12)	0.3315(9)	4.7(6)
C2B	−0.2084(16)	−0.0896(18)	0.4062(13)	9.4(13)
C3B	−0.2796(19)	−0.2117(20)	0.3916(18)	6.1(12)
C3B'	−0.3553(33)	−0.3892(29)	0.2711(25)	3.8(15)
C4B	−0.2603(13)	−0.2564(12)	0.2724(10)	5.1(7)
C5B	0.3376(17)	0.4267(17)	−0.1791(14)	9.2(10)
C6B	0.2576(13)	0.3750(11)	−0.0646(11)	5.0(6)
C7B	−0.1656(11)	−0.1580(10)	0.1760(9)	3.6(5)
N1	0.1641(20)	0.5491(17)	0.3545(15)	13.7(5)
C2	0.1236(23)	0.4100(20)	0.2805(17)	12.5(6)
C3	0.2775(31)	0.6509(26)	0.4530(23)	18.3(9)
C4	0.0796(36)	0.6693(32)	0.3500(27)	22.5(11)
O1	0.0504(40)	0.5173(35)	0.2633(31)	16.9(11)
O2	0.2974(40)	0.5310(34)	0.4060(29)	18.0(10)
H1A	0.3127(0)	0.2667(0)	0.2819(0)	4.6(0)
H2A	0.5354(0)	0.1811(0)	0.3522(0)	5.3(0)
H3A	0.5786(0)	−0.0251(0)	0.2587(0)	6.2(0)
H5A	0.4621(0)	−0.2284(0)	0.0959(0)	5.9(0)
H6A	−0.1741(0)	0.3413(0)	0.1045(0)	5.0(0)
H1B	−0.493(0)	0.1527(0)	0.3621(0)	4.7(0)
H2B	−0.2112(0)	−0.0338(0)	0.5110(0)	7.9(0)
H6B	0.2742(0)	0.4552(0)	0.0215(0)	5.4(0)
H3B	−0.3639(0)	−0.2910(0)	0.4715(0)	4.4(0)
H3B'	0.4367(0)	0.4892(0)	−0.3094(0)	4.9(0)

OCCUPANCY OF C3B = 0.65, OCCUPANCY OF C3B' = 0.35

Table 4 Bond lengths (Å) of $Cu_2(CH_3CO_2)_2(C_7H_6N_2)_2(C_7H_5N_2)_2$

ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH
Cu	Cu	2.747(2)	Cu	N2A	1.968(8)	Cu	N1A	1.964(7)
Cu	N1B	2.229(8)	Cu	01	2.045(6)	Cu	02	2.017(6)
N2A	C6A	1.36(1)	N2A	C7A	1.35(1)	N1A	C1A	1.34(1)
N1A	C7A	1.36(1)	C6A	C5A	1.35(1)	C6A	H6A	1.11(1)
C5A	C4A	1.72(2)	C5A	C3A'	1.38(3)	C5A	H5A	1.13(1)
C4A	C3A	1.11(2)	C4A	C3A'	1.09(2)	C4A	C7A	1.38(1)
C3A	C3A'	1.31(3)	C3A	C2A	1.39(2)	C3A	H3A	1.08(2)
C3A	H2A	1.42(2)	C3A'	H5A	1.77(3)	C2A	C1A	1.37(1)
C2A	H3A	1.62(1)	C2A	H2A	1.07(1)	C1A	H1A	1.12(1)
N2B	C6B	1.43(1)	N2B	C7B	1.38(1)	N2B	HN2B	0.81(1)
N1B	C1B	1.37(1)	N1B	C7B	1.31(1)	C6B	C5B	1.33(2)
C6B	HN2B	1.47(1)	C6B	H6B	1.12(1)	C5B	C4B	1.41(2)
C3B	H5B	1.10(1)	C4B	C3B	1.37(1)	C4B	C7B	1.46(1)
C3B	C2B	1.38(2)	C3B	H3B	1.09(1)	C2B	C1B	1.40(1)
C2B	H2B	1.10(1)	C1B	H1B	1.10(1)	C7B	HN2B	1.65(1)
01	C1C	1.26(1)	02	C1C	1.23(1)	C1C	C2C	1.54(1)
C2C	H2CA	1.04(1)	C2C	H2CB	1.09(1)	C2C	H2CC	1.10(1)
H3A	H2A	0.84(1)						

Table 5 Bond length (Å) of $Ni_2(C_7H_5N_2)_4.2DMF$

ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH
Ni	Ni	2.594(2)	Ni	N1A	1.907(7)	Ni	N2A	1.913(7)
Ni	N1B	1.905(7)	NI	N2B	1.894(7)	N1A	C1A	1.36(1)
N1A	C7A	1.34(1)	N2A	C6A	1.35(1)	N2A	C7A	1.33(1)
C1A	C2A	1.42(1)	C1A	H1A	1.13(3)	C2A	C3A	1.30(1)
C2A	H2A	1.12(3)	C3A	C4A	1.33(1)	C3A	H3A	1.09(3)
C4A	C5A	1.52(1)	C4A	C7A	1.42(1)	C4A	H5A	1.81(3)
C5A	C6A	1.37(1)	C5A	H5A	1.08(3)	C6A	H6A	1.16(3)
N1B	C1B	1.36(1)	N1B	C7B	1.34(1)	N2B	C6B	1.35(1)
N2B	C7B	1.35(1)	C1B	C2B	1.37(1)	C1B	H1B	1.17(3)
C2B	C3B	1.11(2)	C2B	C4B	2.00(2)	C2B	H2B	1.19(3)
C3B	C3B'	1.98(3)	C3B	C4B	1.32(2)	C3B	H3B	1.20(3)
C3B'	C4B	1.24(2)	C3B'	C5B	1.04(3)	C3B'	H3B'	1.05(3)
C4B	C5B	1.77(1)	C4B	C7B	1.43(1)	C5B	C6B	1.38(1)
C5B	H3B'	1.61(3)	C6B	H6B	1.13(3)	N1	C2	1.44(2)
N1	C3	1.49(2)	N1	C4	1.57(3)	N1	01	1.31(3)
N1	02	1.36(3)	C2	01	1.40(3)	C3	02	1.30(3)
C4	01	1.62(4)						

Table 6 Bond angles (deg) of $Cu_2(CH_3CO_2)_2(C_7H_6N_2)_2(C_7H_5N_2)_2$

ATOM1	ATOM2	ATOM3	ANGLE	ATOM1	ATOM2	ATOM3	ANGLE
Cu	Cu	N2A	84.4(2)	Cu	Cu	N1A	84.9(2)
Cu	Cu	N1B	178.7(2)	Cu	Cu	01	79.4(1)
Cu	Cu	02	85.4(2)	N2A	Cu	N1A	169.3(3)
N2A	Cu	N1B	94.9(3)	N2A	Cu	01	90.4(3)
N2A	Cu	02	88.7(3)	N1A	Cu	N1B	95.8(3)
N1A	Cu	01	88.0(3)	N1A	Cu	02	90.1(3)
N1B	Cu	01	99.5(3)	N1B	Cu	02	95.7(3)
01	Cu	02	164.9(2)	Cu	N2A	C6A	128.8(6)
Cu	N2A	C7A	124.1(6)	C6A	N2A	C7A	107.1(8)
Cu	N1A	C1A	126.1(7)	Cu	N1A	C7A	123.5(6)
C1A	N1A	C7A	110.0(8)	N2A	C6A	C5A	119.8(9)
N2A	C6A	H6A	123.0(1)	C5A	C6A	H6A	117.0(1)
C6A	C5A	C4A	96.7(6)	C6A	C5A	C3A'	136.0(1)
C6A	C5A	H5A	135.0(1)	C4A	C5A	C3A'	39.0(1)
C4A	C5A	H5A	129.0(1)	C3A'	C5A	H3A	89.0(1)
C5A	C4A	C3A	127.0(1)	C5A	C4A	C3A'	33.0(1)
C5A	C4A	C7A	102.0(1)	C3A	C4A	C3A'	74.0(1)
C3A	C4A	C7A	131.0(1)	C3A'	C4A	C7A	155.0(2)
C4A	C3A	C3A'	53.0(1)	C4A	C3A	C2A	110.0(1)
C4A	C3A	H3A	169.0(2)	C4A	C3A	H2A	155.0(1)
C3A'	C3A	C2A	162.0(2)	C3A'	C3A	H3A	116.0(2)
C3A'	C3A	H2A	152.0(2)	C2A	C3A	H3A	91.0(1)
C2A	C3A	H2A	44.8(8)	H3A	C3A	H2A	36.3(9)
C5A	C3A'	C4A	88.0(2)	C5A	C3A'	C3A	142.0(2)
C5A	C3A'	H5A	39.4(9)	C4A	C3A'	C3A	54.0(1)
C4A	C3A'	H5A	127.0(2)	C3A	C3A'	H5A	178.0(2)
C3A	C2A	C1A	126.0(1)	C3A	C2A	H3A	41.4(9)
C3A	C2A	H2A	69.0(1)	C1A	C2A	H3A	167.0(1)
C1A	C2A	H2A	166.0(1)	H3A	C2A	H2A	27.7(8)
N1A	C1A	C2A	120.0(1)	N1A	C1A	H1A	119.0(1)
C2A	C1A	H1A	120.0(1)	N2A	C7A	N1A	123.0(8)
N2A	C7A	C4A	114.0(1)	N1A	C7A	C4A	123.0(1)
C6B	N2B	C7B	106.0(1)	C6B	N2B	HN2B	76.0(1)
C7B	N2B	HN2B	94.0(1)	Cu	N1B	C1B	118.6(7)
Cu	N1B	C7B	121.5(7)	C1B	N1B	C7B	117.1(9)
N2B	C6B	C5B	110.0(1)	N2B	C6B	HN2B	32.3(6)
N2B	C6B	H6B	125.0(1)	C5B	C6B	HN2B	108.0(1)
C5B	C6B	H6B	124.0(1)	HN2B	C6B	H6B	119.0(1)
C6B	C5B	C4B	110.0(1)	C6B	C5B	H5B	125.0(1)
C4B	C5B	H5B	125.0(1)	C5B	C4B	C3B	141.0(1)
C5B	C4B	C7B	104.0(1)	C3B	C4B	C7B	114.0(1)
C4B	C3B	C2B	123.0(1)	C4B	C3B	H3B	118.0(1)
C2B	C3B	H3B	119.0(1)	C3B	C2B	C1B	118.0(1)
C3B	C2B	H2B	118.0(1)	C1B	C2B	H2B	124.0(1)
N1B	C1B	C2B	122.0(1)	N1B	C1B	H1B	121.0(1)
C2B	C1B	H1B	117.0(1)	N2B	C7B	N1B	125.0(1)
N2B	C7B	C4B	109.0(1)	N2B	C7B	HN2B	29.2(6)
N1B	C7B	C4B	125.0(1)	N1B	C7B	HN2B	125.1(9)
C4B	C7B	HN2B	101.7(9)	Cu	01	C1C	127.2(6)
Cu	02	C1C	121.9(6)	01	C1C	02	126.0(9)
01	C1C	C2C	116.3(9)	02	C1C	C2C	117.7(9)
C1C	C2C	H2CA	99.0(1)	C1C	C2C	H2CB	117.0(1)
C1C	C2C	H2CC	114.0(1)	H2CA	C2C	H2CB	110.0(1)
H2CA	C2C	H2CC	109.0(1)	H2CB	C2C	H2CC	107.0(1)
C5A	H5A	C3A'	51.0(1)	C3A	H3A	C2A	58.0(1)
C3A	H3A	H2A	94.0(1)	C2A	H3A	H2A	36.0(1)
C3A	H2A	C2A	6.0(1)	C3A	H2A	H3A	50.0(1)
C2A	H2A	H3A	116.0(1)	N2B	HN2B	C6B	71.0(1)
N2B	HN2B	C7B	57.0(1)	C6B	HN2B	C7B	91.9(9)

Table 7 Bond angles (deg) of $Ni_2(C_7H_5N_2)_4.2DMF$

ATOM1	ATOM2	ATOM3	ANGLE	ATOM1	ATOM2	ATOM3	ANGLE
Ni	Ni	N1A	89.4(2)	Ni	Ni	N2A	84.5(2)
Ni	Ni	N1B	87.5(2)	Ni	Ni	N2B	86.6(2)
N1A	Ni	N2A	173.9(3)	N1A	Ni	N1B	88.3(3)
N1A	Ni	N2B	89.3(3)	N2A	Ni	N1B	90.7(3)
N2A	Ni	N2B	91.1(3)	N1B	Ni	N2B	173.7(3)
Ni	N1A	C1A	123.9(6)	Ni	N1A	C7A	116.7(5)
C1A	N1A	C7A	119.3(7)	Ni	N2A	C6A	129.1(6)
Ni	N2A	C7A	122.2(6)	C6A	N2A	C7A	106.7(7)
N1A	C1A	C2A	116.8(9)	N1A	C1A	H1A	124.(1)
C2A	C1A	H1A	119.(1)	C1A	C2A	C3A	123.5(9)
C1A	C2A	H2A	117.(1)	C3A	C2A	H2A	119.(1)
C2A	C3A	C4A	121.(1)	C2A	C3A	H3A	116.(1)
C4A	C3A	H3A	123.(1)	C3A	C4A	C5A	139.(1)
C3A	C4A	C7A	118.(1)	C3A	C4A	H5A	102.(1)
C5A	C4A	C7A	103.7(8)	C5A	C4A	H5A	37.(1)
C7A	C4A	H5A	140.(1)	C4A	C5A	C6A	103.5(8)
C4A	C5A	H5A	86.(1)	C6A	C5A	H5A	170.(1)
N2A	C6A	C5A	113.2(8)	N2A	C6A	H6A	127.(1)
C5A	C6A	H6A	120.(1)	N1A	C7A	N2A	127.1(8)
N1A	C7A	C4A	121.8(8)	N2A	C7A	C4A	111.0(8)
Ni	N1B	C1B	127.5(6)	Ni	N1B	C7B	118.8(6)
C1B	N1B	C7B	113.7(8)	Ni	N2B	C6B	129.5(6)
Ni	N2B	C7B	120.0(5)	C6B	N2B	C7B	110.4(7)
N1B	C1B	C2B	116.(1)	N1B	C1B	H1B	116.(1)
C2B	C1B	H1B	126.(1)	C1B	C2B	C3B	137.(1)
C1B	C2B	C4B	98.3(9)	C1B	C2B	H2B	106.(1)
C3B	C2B	C4B	38.(1)	C3B	C2B	H2B	118.(1)
C4B	C2B	H2B	156.(1)	C2B	C3B	H3B'	148.(1)
C2B	C3B	C4B	110.(1)	C2B	C3B	H3B	125.(2)
C3B'	C3B	C4B	37.9(9)	C3B'	C3B	H3B	87.(1)
C4B	C3B	H3B	125.(2)	C3B	C3B'	C4B	41.(1)
C3B	C3B'	C5B	143.(2)	C3B	C3B'	H3B'	116.(2)
C4B	C3B'	C5B	102.(2)	C4B	C3B'	H3B'	157.(3)
C5B	C3B'	H3B'	101.(2)	C2B	C4B	C3B	31.4(8)
C2B	C4B	C3B'	133.(1)	C2B	C4B	C5B	167.4(7)
C2B	C4B	C7B	92.4(7)	C3B	C4B	C3B'	101.(1)
C3B	C4B	C5B	136.(1)	C3B	C4B	C7B	124.(1)
C3B'	C4B	C5B	35.(1)	C3B'	C4B	C7B	135.(1)
C5B	C4B	C7B	100.0(7)	C3B'	C5B	C4B	43.(1)
C3B'	C5B	C6B	141.(1)	C3B'	C5B	H3B'	40.(1)
C4B	C5B	C6B	98.1(9)	C4B	C5B	H3B'	83.(1)
C6B	C5B	H3B'	178.(1)	N2B	C6B	C5B	118.(1)
N2B	C6B	H6B	123.(1)	C5B	C6B	H6B	120.(1)
N1B	C7B	N2B	127.0(8)	N1B	C7B	C4B	119.3(8)
N2B	C7B	C4B	113.7(8)	C2	N1	C3	145.(1)
C2	N1	C4	128.(1)	C2	N1	01	61.(1)
C2	N1	02	91.(1)	C3	N1	C4	86.(1)
C3	N1	01	153.(2)	C3	N1	02	54.(1)
C4	N1	01	68.(1)	C4	N1	02	140.(1)
01	N1	02	150.(2)	N1	C2	01	55.(1)
N1	C3	02	58.(1)	N1	C4	01	49.(1)
N1	01	C2	64.(1)	N1	01	C4	64.(1)
C2	01	C4	128.(2)	N1	02	C3	68.(2)
C4A	H5A	C5A	57.(1)	C3'	H3B'	C5B	39.(1)

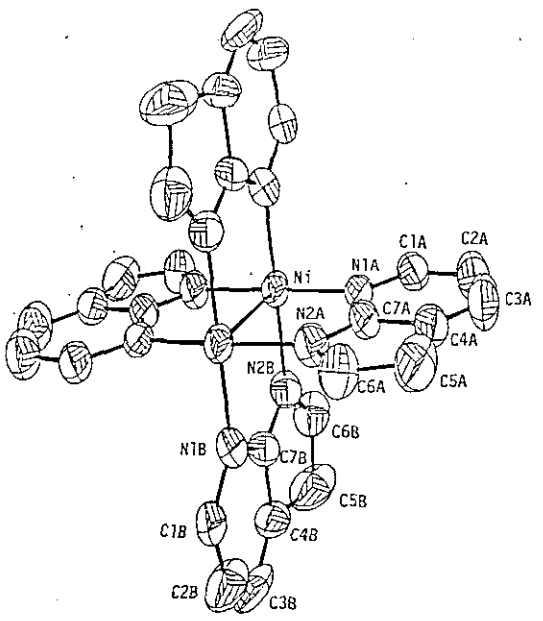


Fig. 4 Molecular structure of $Ni_2(C_7H_5N_2)_4.2DMF$

pocking dmf solvent. The Ni-Ni distance is 2.594(2); Ni-N, 1.905(7) Å. These two molecules lie on crystallography inversion centers.

Both of these molecules exhibit 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)' atom were refined.

Another indication of the disorder of ligand is the temperature factors of the atoms N(1), N(2), C(7) atoms having Biso values around 3 to 4 (Å^2) and the remaining atoms of ligand have higher Biso values (5 – 9 Å^2).

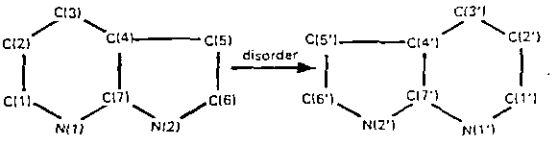


Table 8 Comparison of the structure and magnetic interaction of dinuclear cupper complexes

	Structure type	Cu-Cu distance	Magnetism BM*	2J(cm^{-1})	Reference
$[Cu(dpt)_2]_2$	dimer	2.44 A	diamagnestim		13
$[Cu(C_5H_4NO)_2(dmso)]_2$	dimer	2.588			23
$[Cu(DMB^a)(OAc)(H_2O)]_2$	dimer	2.597		−325	19
$[Cu(DMB)_2(H_2O)]_2$	dimer	2.620		−250	19
$[Cu(PAc)_2(H_2O)]_2$	dimer	2.64	1.39	−286	15
$[Cu(OAc)_2py]_2$	dimer	2.64		−325	17, 22
$[Cu(OAc)(C_7H_5N_2)(C_7H_6N_2)]_2$	dimer	2.747	1.49	−232	this work
$[Cu(C_7H_5N_2)_2(dmf)]_2$	dimer	2.782	1.27	−361	12
$[Cu(adH^b)_2(H_2O)_2]_2(ClO_4)_4$	dimer	2.95	1.45		24
$[Cu(ad^c)_2(H_2O)_2]_2$	dimer	2.95		−257	25, 26
$[Cu(ap^d)_2(H_2O)_4]_2$	dimer	2.95		−185	27, 28
$[Cu(hpH^e)_2(H_2O)]_2Cl_4$	dimer	3.024	1.38	−200	27,28
$[Cu(apH^f)_2\,3/2(H_2O)]_2Cl_2$	dimer	3.066	1.39	−206	27, 28
$[Cu(ade^b)_2Cl]_2Cl_2.6H_2O$	dimer	3.066	1.45		29
$[Cu(C_2H_5CO_2)_2.P\text{-}tol]_2$	chain	3.27		−105	30

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 = 9.27 10^{-24}JT^{-1}

Table 9 Comparison of some structural parameters of dinuclear cupper and nickel complexes

(M-M)m is the distance in the pure metal; (M-M)c is the distance in the compound.
All distance in Å and angles in degrees

Compound	Ligand bite	Interplanar spacing	Average twist angle	(M-M)c distance	(M-M)m distance	Reference
$Ni_2(dpt)_4$	2.23	2.17	16	2.395	2.50	13
$Ni_2(SOCPh)_4.EtOH$	2.61	2.50	23	2.50		20
$Ni_2(S_2CCH_2Ph)_4$	3.01	2.82	20	2.56		21
$Ni_2(C_7H_5N_2)_4.2DMF$	2.396	2.396	0	2.594		this work
$Cu_2(dpt)_4$	2.23	2.13	17	2.441	2.56	13
$Cu_2(DMB)_2(OAc)_2(H_2O)_2$	2.239	2.234	0	2.597		19
	2.228 (OAc)					
$Cu_2(OAc)_4(H_2O)_2$*	2.233	2.233	0	2.614		16
$Cu_2(DMB)_4(H_2O)_2$	2.227	2.227	0	2.620		19
$Cu_2(OAc)_4(H_2O)_2$	2.20	2.20	0	2.64		15
$Cu_2(OAc)_2(C_7H_5N_2)_2(C_7H_6N_2)_2$	2.381	2.296	0	2.747		this work
	2.210 (OAc)					
$Cu_2(C_7H_5N_2)_4(DMF)_2$	2.358	2.358	0	2.782		12

dpt = 1,3-diphenyltriazene
DMB = 2,6-methoxybenzoato
* neutron strudy

DISCUSSION

The Cu-Cu distance of $[Cu_2(OAc)_2L_2(HL)_2]$ (2.747 Å) is longer than that of $[Cu_2(dpt)_4]$[13] (2.40 Å) and $[Cu_2(OAc)_4(H_2O)_2]$[15] (2.64 Å), but shorter than that of $[Cu_2(C_7H_5N_2)_4(dmf)_2]$[12] (2.782 Å) and $[Cu_2(Ad)_4(H_2O)_2]$[18] (2.95 Å). The comparison of the metal-metal distance and magnetism for the dimeric structure of copper complexes are listed in Table 8. The Ni-Ni distance of $[Ni_2L_4.2DMF]$ (2.594 Å) is longer than that of $[Ni_2(dpt)_4]$[13] (2.395 Å), $[Ni_2(SOCPh)_4.EtOH]$[20] (2.50 Å), and $[Ni_2(S_2CCH_2Ph)_4]$[21] (2.56 Å).

The metal-metal distance and distinct twist away from the eclipsed conformation for some dimeric metal complexes are summarized in Table 9. As explained by Corbett et. al.[13], the metal-metal distance is a compromise between thd binding force between metal atoms and the repulsive forces between the filled d orbitals, δ (d_{xy}), centered on each metal atoms. Furthermore, it is suggested that the small variations of metal-metal distance are attributable to the different bonding ability of chelating atoms and π - electron delocalization of ligands.

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REFERENCES

1. Pang S., Wang Y., Chung M., Le Page Y. and Gabe E.; *J. Chem. Soc., Chem. Commun.* **1981**, 329.
2. Peng S., Wang Y. and Chiang C. K.; *Acta Crystallogr.* **1984**, Sect. C, *40*, 1541.
3. Peng S., Chen C.T., Liaw D. S., Chen C. I. and Wang Y.; *Inorg. Chim. Acta* **1985**, *101*, L31.
4. Peng S., Liaw D. S., Wang Y. and Simon A.; *Angew. Chem. Int.* Ed. Engl. **1985**, *24*, 210.
5. Peng S., Ibers J., Millar M. and Holm P.; *J. Am. Chem. Soc.* **1972**, *98*, 1382.
6. Peng S., Goedken V. L.; *J. Am. Chem. Soc.* **1976**, *98*, 8500.
7. Collman J. P., Barnes C. E., Swepston P. N. and Ibers J. A.; *J. Am. Chem. Soc.* **1984**, *106*, 3500.
8. Brookes R. W. and Martin R. L.; *Aust. J. Chem.* **1975**, *28*, 1363.
9. Brookes R. W. and Martin R. L.; *Aust. J. Chem.* **1974**, *27*, 1569.
10. Brookes R. W. and Martin R. L.; *Inorg. Chem.* **1975**, *14*, 528.
11. Cotton F. A., Lay D. G. and Millar M.; *Inorg. Chem.* **1978**, *17*, 187.
12. Lin Y. and Peng S.; *Acta Crystallogr.*, **1986**, *C42*, 1725.
13. Corbett M., Hoskins B. F., Mcleod N. J. and O'Day B. P.; *Aust. J. Chem.* **1975**, *28*, 2377.
14. Corbett M., Hoskins B. F.; *Aust. J. Chem.* **1974**, *27*, 665.
15. Van Niekerk J. N., Schoening F. R. L.; *Acta Crystallogr.*, **1953**, *6*, 227.
16. Brown G. M., Chidambaram R.; *Acta Crystallogr.*, **1973**, *B29*, 2393.
17. Kokot E., Martin R. L.; *Inorg. Chem.* **1964**, *3*, 1306.
18. Lee F. L., Gage E. J.; "The NRC PDP-11 Crystal Structure System", **1981**.
19. Erre L. S.; Micera G., Piu P., Cariati F. and Ciani G.; *Inorg. Chem.* **1985**, *24*, 2297.
20. Bonamico M., Dessy G., Fares V., *Chem. Commun.* **1969**, 697; Meison G. A., Greene P. T., Bryan R. F., *Inorg. Chem.* **1970**, *9*, 1116.
21. Bonamico M., Dessy G., Fares V., *Chem. Commun. 19*, 1106.
22. Bacriay G. A., Kennard C. H. L.; *J. Chem. Soc. Bal.* **1961**, 5244.
23. Peng S., Liaw D., Yeh S.; *Bull. Inst. Chem. Aca. Sinica* **1987**, *34*, 50.
24. Terzis A., Beavchamp A. L., Riversist R.; *Inorg. Chem.* **1973**, 12, 5, 1166.
25. Goodgame D. M. L., Price K. A.; *Nature* (London), **1968**, *220*, 783.
26. Sletten E.; *Acta Crystallogr.* **1969**, *25*, 1480.
27. Venner Weiss, Rand; *Phys. Chem.* **1963**, *333*, 169.
28. Askawa T., Inoue M., Hara K., Kubo M.; *Bull. Chem. Soc. Tpn.* **1972**, *45*, 1054.
29. Meester P., Skaski K. C.; *J. Chem. Soc.* **1971**, *A*, 2167.
30. Yawney D. B. W., Moreland J. A., Doedens R. T.; *J. Am. Chem. Soc.* **1973**, *95*, 1164.