(III) amine complexes. The much greater reactivity of *trans*-$[Ru(L)Cl_2]^+$ than the corresponding *trans*-$[Ru(L)(OH)Cl]^+$, as measured by the ratio of their corresponding rate constants at 25.0 °C (L = cyclam, 5.0×10^3; L = teta, 3.2×10^2; and L = tetb, 2.3×10^2), also follows the same pattern as that of the well-studied *trans*-$[CO(L)Cl_2]^+$ and *trans*-$[Co(L)(OH)Cl]^+$ systems with the corresponding kinetic ratios of 1.5×10^4 (L = cyclam)[21,24] and 5.5×10^3 (L = $(en)_2$).[25]

Acknowledgment. We thank the Committee on Research and Conference Grants of the University of Hong Kong for support.

Registry No. $[Ru(teta)Cl_2]^+ClO_4^-$, 76792-47-1; $[Ru(teta)Br_2]^+ClO_4^-$, 76792-49-9; $[Ru(tetb)Cl_2]^+ClO_4^-$, 76705-22-1; $[Ru(tetb)Br_2]^+ClO_4^-$, 76705-24-3; $[Ru(cyclam)Br_2]^+Br^-$, 74202-83-8; $[Ru(cyclam)(OH)Cl]^+$, 85282-36-6; $[Ru(teta)(OH)Cl]^+$, 85282-37-7; $[Ru(tetb)(OH)Cl]^+$, 85317-75-5; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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Synthesis, Structure, and Magnetism of a New Type of π-Molecular Complex Containing Binuclear Copper(II) Complexes and Benzene: Bis[2,2-dimethyl-7-(phenylimino)-3,5,7-octanetrionato]dicopper(II)–Benzene and Bis[2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper(II)–Bis(benzene)

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The title compounds have been crystallized and examined by X-ray diffraction techniques. The structure of $Cu_2(PAAan)_2{\cdot}C_6H_6$ consists of stacks of alternating bis[2,2-dimethyl-7-(phenylimino)-3,5,7-octanetrionato]dicopper(II), $Cu_2(PAAan)_2$, and benzene molecules in an ADAD... pattern. Crystal data are as follows: *C*2/*m*, *a* = 19.001 (9) Å, *b* = 6.516 (3) Å, *c* = 15.802 (6) Å, *β* = 113.36 (3)°, R_1 = 0.044, R_2 = 0.058. The structure of $Cu_2(PAApnan)_2{\cdot}2C_6H_6$ consists of benzenes positioned directly above and below the center of the bis(2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper(II) molecule. These units are stacked in a DADDAD... pattern. Crystal data are as follows: *C*2/*c*, *a* = 15.312 (3) Å, *b* = 10.399 (2) Å, *c* = 23.743 (4) Å, *β* = 91.82 (1)°, R_1 = 0.039, R_2 = 0.048. In $Cu_2(PAAan)_2{\cdot}C_6H_6$ the planes of the alternating benzenes and metal complexes are parallel and separated by 3.258 (2) Å. In $Cu_2(PAApnan)_2{\cdot}2C_6H_6$, the two benzenes and each complex molecule are effectively parallel (dihedral angle 1.4°) and separated by 3.262 (8) Å. The interplanar spacing between benzene molecules associated with different binuclear chelates within the same stack is 3.860 (8) Å. These values are consistent with those found in a great many organic π-molecular complexes and are indicative of a weak donor–acceptor interaction between the benzene and binuclear Cu(II) complex. In both compounds the copper atoms and the donor atoms are coplanar, and both compounds are diamagnetic at room temperature. These results support the conclusion that coplanarity is a structural prerequisite for optimal antiferromagnetic exchange.

Introduction

Several authors[1] have demonstrated relationships between molecular structure and magnetic exchange in binuclear copper(II) complexes. One family of such complexes consists of the bis(1,3,5-triketonato)dicopper chelates and their Schiff base derivatives.[2] Previous X-ray crystal structure determinations[3] of bis(1,3,5-triketonato)dicopper(II) complexes showed that these molecules contain one axial ligand per copper, resulting in displacement of the copper from the plane of the equatorial ligands in typical 5-coordinate fashion. Thus, all magnetic-exchange–structural studies on these compounds to date have contained the complicating factor that the coppers are not in the simplest site symmetry. In order to present the simplest case for magnetic exchange between the copper ions, one would prefer that the coppers and donor atoms be coplanar. The binuclear Cu(II) complexes prepared from 1,3,5-triketones in which one terminal carbonyl oxygen has been replaced by an aniline (or substituted aniline) nitrogen were isolated as very small crystals without adducting ligands. Thus, these binuclear complexes seemed an excellent class of compounds for structural–magnetic studies since it appeared likely that the two copper atoms and the six donor atoms were coplanar.

In order to determine the structure of a binuclear triketonate without axial ligation, two complexes, bis[2,2-dimethyl-7-phenylimino-3,5,7-octanetrionato]dicopper, $Cu_2(PAAan)_2$, and bis[2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper, $Cu_2(PAApnan)_2$, were recrystallized from dichloromethane, chloroform, and benzene. Crystals of $Cu_2(PAAan)_2$ isolated from CH_2Cl_2 and $CHCl_3$ solutions proved to be twinned. However, both compounds form excellent crystals from benzene and both contain benzenes of crystallization. Interestingly, the stoichiometries of the two are different. The first crystallizes with one benzene per molecule, $Cu_2(PAAan)_2{\cdot}C_6H_6$, and the second with two per molecule, $Cu(PAApnan)_2{\cdot}2C_6H_6$. Both are unusually stable with respect to loss of benzene.

[†] Stanford University.

[‡] Wayne State University.

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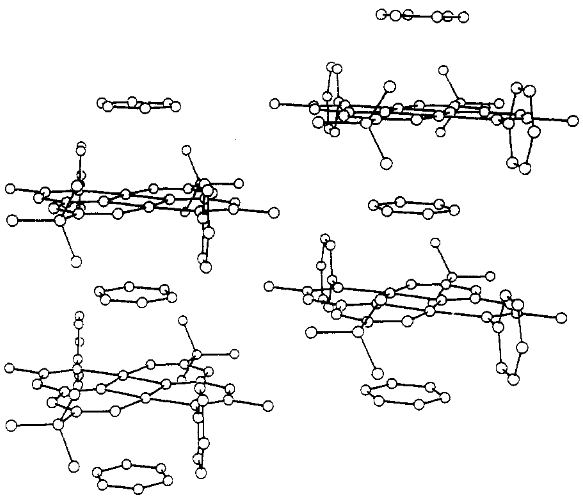

Figure 1. Packing diagram of $Cu_2(PAAan)_2{\cdot}C_6H_6$.

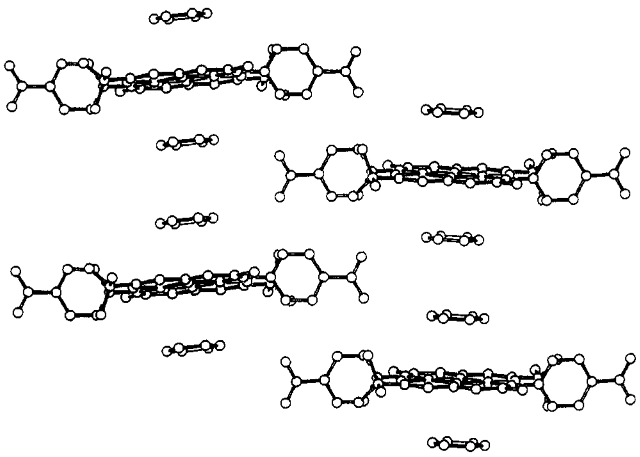

Figure 2. Unit cell of $Cu_2(PAApnan)_2{\cdot}2C_6H_6$.

Experimental Section

Preparation of $H_2AApnan$. We prepared 2,2-dimethyl-3,5,7-octanetrione, H_2PAA, by the Claisen-type condensation of methyl 2,2-dimethylpropionate with 2,4-pentanedione using NaH in refluxing THF.[4] A solution of 6.2 mL (30 mmol) of H_2PAA, 3 drops of concentrated H_2SO_4, and 4.2 g (30 mmol) of 4-nitroaniline in 125 mL of benzene was refluxed for $3^1/_2$ h in a 250-mL flask fitted with a Dean–Stark trap. The benzene was removed by evaporation under reduced pressure. An orange solid (9.53 g) was obtained and used without further purification.

Preparation of H_2PAAan. A solution prepared by adding 1.50 mL (1.53 g, 0.016 mol) of aniline and 3.33 mL (3.00 g, 0.16 mol) of H_2PAA to 25 mL of hot methanol was heated to boiling and refluxed for about 30 min. Removal of the solvent yielded an oil. The ligand was used in this form without further purification.

Preparation of $Cu_2(PAAan)_2$. The ligand described above was added dropwise to a solution of 3.25 g (0.016 mol) of cupric acetate hydrate in 250 mL of boiling methanol. The solution turned dark green, and a precipitate formed. This mixture was refluxed for 20 min and filtered hot, and the product was isolated as small dark green microcrystals. It is sparingly soluble in CH_3OH and soluble in $CHCl_3$, C_6H_6, and CH_2Cl_2; mp 233 °C. Anal. Calcd for $Cu_2C_{32}H_{38}N_2O_4$: C, 59.89; H, 5.97; N, 4.36. Found: C, 59.55; H, 6.09; N, 4.20.

Preparation of $Cu_2(PAApnan)_2$. A slurry of 2.26 g (7.42 mmol) of $H_2PAApnan$ in $CHCl_3$ was added to a refluxing solution of 1.66 g (7.44 mmol) of $CuBr_2$ and 3 mL (21 mmol) of triethylamine in 150 mL of absolute methanol distilled from Mg metal. Dark olive microcrystals of $Cu_2(PAApnan)_2$ formed rapidly, were filtered after 30 min, and placed overnight in a vacuum desiccator: mp 234–235 °C; yield 1.73 g. Anal. Calcd for $Cu_2C_{32}H_{36}N_4O_8$: C, 52.53; H, 5.15; N, 7.65. Found: C, 52.17; H, 4.95; N, 7.43.

Preparation of $Cu_2(PAAan)_2{\cdot}C_6H_6$ and $Cu_2(PAApnan)_2{\cdot}2C_6H_6$. In each case approximately 20 mg of the complex was dissolved in 3 mL of hot reagent grade benzene in a 5-mL beaker. The mouth of the beaker was covered by a paraffin sheet with a 2 mm diameter hole. The benzene was allowed to evaporate for several days until crystals suitable for X-ray diffraction had formed. Anal. Calcd for $Cu_2(PAApnan)_2{\cdot}2C_6H_6$, $Cu_2C_{44}H_{48}N_4O_8$: C, 59.52; H, 5.45; N, 6.31. Found: C, 59.42; H, 5.41; N, 6.30.

Crystallographic Data. Single-crystal X-ray structure determinations of the title compounds were undertaken. All pertinent information relating to these determinations may be found in Table I. Atomic parameters are contained in Tables II and III and selected distances and angles in Table IV.

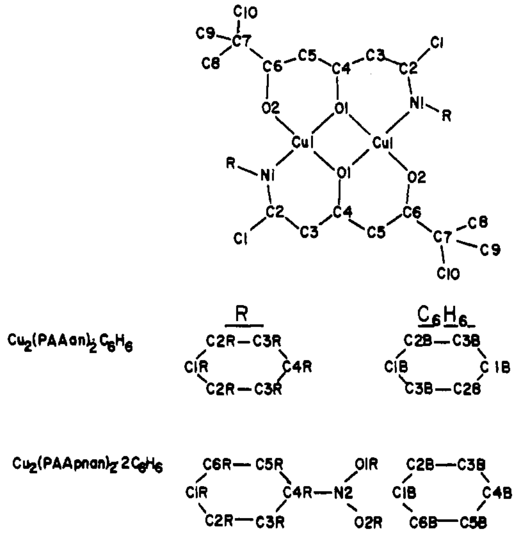

Figure 3. Atom-numbering scheme for $Cu_2(PAAan)_2{\cdot}C_6H_6$ and $Cu_2(PAApnan)_2{\cdot}2C_6H_6$.

Magnetic Studies. Magnetic susceptibility measurements were made with use of normal Faraday balance techniques with $Hg[Co(SCN)]_4$ as a standard. Pascal's constants were used for diamagnetic corrections.

Results

The structural results show a profound difference in the solid-state structures of the two compounds. The simpler compound of the two, $Cu_2(PAAan)_2{\cdot}C_6H_6$, is composed of staggered stacks of alternating binuclear Cu(II) chelate molecules and benzene molecules (Figure 1) in which the benzenes sit equidistant between two chelate molecules. The benzenes are centered above and below the inversion center of the complex with a distance of 3.258 (2) Å between the mean position of the benzene carbons and the center of the chelate, thereby forming an ADADAD arrangement, where A is the chelate molecule and D is benzene.

The nitro derivative, $Cu_2(PAApnan)_2{\cdot}2C_6H_6$, on the other hand, has two benzenes associated with each chelate molecule. It also is composed of staggered stacks, but in this case in a DADDAD pattern. The unit cell (Figure 2) contains four molecules of the binuclear chelate and eight molecules of benzene. Units consisting of one chelate molecule and two benzenes sit on an inversion center designated as (d) in the Wycoff notation. The benzene molecules are centered above and below the chelate inversion center with a distance of 3.262 (8) Å between the mean position of the benzene carbon atoms and the center of the chelate. The interplanar spacing between neighboring benzene molecules located in the same stack but

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Table I. X-ray Experimental Data

	$Cu_2(PAAan)_2 \cdot C_6H_6$	$Cu_2(PAApnan)_2 \cdot 2C_6H_6$
radiation used	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
space group	$C2/m$	$C2/c$
Z	2	4
ρ_{obsd}(flotation), g/cm^3		1.408
ρ_{calcd}, g/cm^3	1.336	1.385
cell constants ($\lambda = 0.71069$ Å)		
a, Å	19.001 (9)	15.312 (3)
b, Å	6.516 (3)	10.399 (2)
c, Å	15.802 (6)	26.743 (4)
β, deg	113.36 (3)	91.82 (1)
V, Å^3	1796 (1)	4258 (2)
data collection		
type of scan	$\theta/2\theta$	$\theta/2\theta$
scan range, deg	K$\alpha_1 - 1.125$ to K$\alpha_2 + 1.125$	K$\alpha_1 - 1.0$ to K$\alpha_2 + 1.0$
scan rate, deg/min	variable, 2–5	variable, 2–30
bkgd as a part of scan time	0.50	0.25
collection region	$+h, +k, \pm l$	$+h, +k, \pm l$
2θ limits, deg	4–55	3–50
reflctns measd	2642	4165
std reflctns	$(00\bar{5}), (800), (\bar{1}30)$	(602), (040), (0,0,10)
how often measd	every 100 measmts	every 60 measmts
% decay	20	negligible
data reduction		
corrections[a] applied	Lp and decay	Lp
$\sigma(F_o^2)$[b]	$(\sigma_c^2 + 0.05F_o^2)^{1/2}$	$(\sigma_c^2 + 0.05F_o^2)^{1/2}$
obsd reflctn	$F_o^2 > 3\sigma(F_o^2)$	$F_o^2 > 3\sigma(F_o^2)$
unique obsd reflctns	1627	2394
absorption		
μ, cm^{-1}	12.2	10.975
correction made	no	no
solution method[a]	F^2 Patterson, F_o Fourier	$(E^2 - 1)$ Patterson, $F_o - F_c$ Fourier
H atoms		
how located	calcd	calcd
bond distance, Å	0.98	0.98
spatial arrangement	sp^2 and sp^3	sp^2 and sp^3
temp factor, Å^2	$B_H = B_C + 1.0$	$B_H = B_C + 1.0$
refinement		
method	full-matrix least squares	full-matrix least squares
wts	$w = [1/\sigma(F_o)]^2$	$w = [1/\sigma(F_o)]^2$
quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
non-H atoms	anisotropic	anisotropic
H atoms	fixed	fixed
variable parameters	130	262
R_1[c]	0.044	0.039
R_2[d]	0.058	0.048
S[e]	1.713	1.316
$\lvert\Delta\rho_{max}\rvert$, e/Å^3	0.88	0.16
scattering factors[f]	ref 6–8	ref 6, 8
unusual features		rotational disorder in benzene molecules

[a] Reference 9 gives data reduction and programming details for $Cu_2(PAApnan)_2 \cdot 2C_6H_6$. [b] σ_c is from counting statistics. [c] $R_1 = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$. [d] $R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$. [e] $S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variable parameters. [f] Scattering factors included the anomalous components $\Delta f'$ and $\Delta f''$ for Cu in $Cu_2(PAAan)_2 \cdot C_6H_6$ and for all non-hydrogen atoms in $Cu_2(PAApnan)_2 \cdot 2C_6H_6$.

Table II. Atomic Coordinates for $Cu_2(PAAan)_2 \cdot C_6H_6$[a]

atom	x	y	z
Cu(1)	0.06107 (3)	0	0.09798 (3)
O(1)	0.0495 (2)	0	−0.0289 (2)
O(2)	−0.0530 (2)	0	−0.2121 (2)
N(1)	0.1713 (2)	0	0.1467 (2)
C(1)	0.2982 (3)	0	0.1385 (4)
C(2)	0.2118 (3)	0	0.0947 (3)
C(3)	0.1801 (3)	0	−0.0021 (3)
C(4)	0.1030 (3)	0	−0.0618 (3)
C(5)	0.0824 (3)	0	−0.1583 (3)
C(6)	0.0096 (3)	0	−0.2258 (3)
C(7)	−0.0041 (3)	0	−0.3281 (3)
C(8)	0.0665 (4)	0	−0.3468 (4)
C(9)	−0.0502 (5)	−0.1791 (14)	−0.3714 (4)
C(1)R	0.2127 (2)	0	0.2460 (3)
C(2)R	0.2317 (2)	0.1795 (7)	0.2929 (2)
C(3)R	0.2724 (3)	0.1797 (9)	0.3896 (3)
C(4)R	0.2923 (4)	0	0.4356 (4)
C(1)B	0.0774 (4)	0.5000	0.0239 (6)
C(2)B	0.0484 (4)	0.5000	0.0904 (5)
C(3)B	−0.0279 (5)	0.5000	0.0679 (6)

[a] The standard deviations in parentheses refer to the least significant digits.

Table III. Atomic Coordinates for $Cu_2(PAApnan)_2 \cdot 2C_6H_6$[a]

atom	x	y	z
Cu(1)	0.23857 (3)	0.23960 (4)	0.44366 (1)
O(1)	0.1734 (1)	0.2385 (2)	0.50373 (8)
O(2)	0.1804 (1)	0.2571 (3)	0.60737 (8)
O(1)R	0.2315 (3)	0.1367 (4)	0.17594 (11)
O(2)R	0.2049 (3)	0.3366 (3)	0.17385 (11)
N(1)	0.1369 (2)	0.2208 (3)	0.4000 (1)
N(2)	0.2088 (2)	0.2343 (4)	0.1955 (1)
C(1)	−0.0191 (3)	0.1968 (5)	0.3787 (2)
C(2)	0.0560 (2)	0.2096 (4)	0.4163 (1)
C(3)	0.0346 (2)	0.2081 (4)	0.4664 (1)
C(4)	0.0882 (2)	0.2227 (4)	0.5085 (1)
C(5)	0.0536 (2)	0.2216 (4)	0.5570 (1)
C(6)	0.0967 (2)	0.2398 (4)	0.6013 (1)
C(7)	0.0494 (2)	0.2464 (4)	0.6510 (1)
C(8)	0.0952 (3)	0.1585 (5)	0.6887 (2)
C(9)	0.0555 (3)	0.3844 (5)	0.6689 (2)
C(10)	−0.0469 (3)	0.2065 (6)	0.6462 (2)
C(1)R	0.1498 (2)	0.2236 (4)	0.3476 (1)
C(2)R	0.1400 (3)	0.3361 (4)	0.3209 (1)
C(3)R	0.1568 (3)	0.3397 (4)	0.2705 (1)
C(4)R	0.1843 (2)	0.2293 (4)	0.2481 (1)
C(5)R	0.1933 (3)	0.1160 (4)	0.2734 (1)
C(6)R	0.1760 (3)	0.1144 (4)	0.3238 (1)
C(1)B	0.2797 (5)	−0.0700 (5)	0.4532 (2)
C(2)B	0.3574 (4)	−0.0557 (6)	0.4753 (2)
C(3)B	0.3641 (4)	−0.0465 (6)	0.5254 (3)
C(4)B	0.2951 (4)	−0.0496 (5)	0.5524 (2)
C(5)B	0.2160 (4)	−0.0606 (6)	0.5305 (2)
C(6)B	0.2083 (4)	−0.0718 (6)	0.4810 (3)

[a] The standard deviations in parentheses refer to the least significant digits.

associated with different $Cu_2(PAApnan)_2$ molecules is 3.860 (8) Å. The benzene and chelate planes are very nearly parallel with a dihedral angle of 1.4°.

Most bond lengths and angles in the $Cu_2(PAAan)_2$ and $Cu_2(PAApnan)_2$ molecules are very similar, as seen in Table IV. The atom-numbering scheme is shown in Figure 3. A small and possibly significant difference does exist, however, between the C(1)R–N(1) distances. In $Cu_2(PAAan)_2$ this distance is 1.449 (5) Å while in $Cu_2(PAApnan)_2$ it is 1.422 (4) Å. It is possible that the shortened C(1)R–N(1) bond in $Cu_2(PAApnan)_2$ is due to the electron-withdrawing effect of the p-NO_2 group.

A significant difference exists between the structures in that $Cu_2(PAAan)_2$ is constrained to sit on a mirror plane while $Cu_2(PAApnan)_2$ is not. Deviations from coplanarity occur among the carbon atoms of the ligand backbone in $Cu_2(PAApnan)_2$, but they are small. The Cu(II) ions deviate from the plane of the donor atoms by less than 0.01 Å. The plane of the six carbon atoms in the p-nitrophenyl group in $Cu_2(PAApnan)_2$ forms a dihedral angle of 82.4° with the plane of the $Cu_2O_4N_2$ chelate core, while the corresponding angle in $Cu_2(PAAan)_2$ is 90°. The Cu···Cu distance is 3.046 (2) Å in $Cu_2(PAAan)_2$ and 3.030 (1) Å in $Cu_2(PAApnan)_2$.

Table IV. Bond Lengths (Å) and Bond Angles (deg) in $Cu_2(PAAan)_2$ and $Cu_2(PAApnan)_2$

	$Cu_2(PAAan)_2\cdot C_6H_6$	$Cu_2(PAApnan)_2\cdot 2C_6H_6$		$Cu_2(PAAan)_2\cdot C_6H_6$	$Cu_2(PAApnan)_2\cdot 2C_6H_6$
Cu(1)-O(1)	1.928 (3)	1.918 (2)	C(1)R-N(1)	1.449 (5)	1.422 (4)
-O(1)^a	1.946 (3)	1.931 (2)	-C(2)R	1.355 (5)	1.376 (5)
-O(2)^a	1.870 (3)	1.874 (2)	-C(2)R^b	1.355 (5)	
-N(1)	1.924 (4)	1.926 (3)	-C(6)R		1.368 (5)
C(2)-C(1)	1.508 (6)	1.509 (5)	C(3)R-C(2)R	1.412 (5)	1.379 (5)
-N(1)	1.331 (6)	1.333 (4)	-C(4)R	1.351 (6)	1.368 (5)
-C(3)	1.405 (6)	1.390 (5)	C(5)R-C(4)R		1.363 (5)
C(4)-C(3)	1.393 (6)	1.381 (5)	-C(6)R		1.380 (4)
-O(1)	1.313 (5)	1.326 (4)	N(2)R-C(4)R		1.469 (4)
-C(5)	1.416 (6)	1.415 (4)	-O(1)R		1.198 (4)
C(6)-C(5)	1.372 (6)	1.352 (4)	-O(2)R		1.212 (4)
-O(2)	1.291 (6)	1.299 (4)	C(1)B-C(2)B	1.367 (10)	1.321 (10)
-C(7)	1.533 (6)	1.537 (4)	-C(3)B^c	1.381 (11)	
C(7)-C(8)	1.484 (9)	1.516 (5)	-C(6)B		1.340 (10)
-C(9)	1.457 (8)	1.514 (6)	C(3)B-C(2)B	1.348 (10)	1.343 (10)
-C(9)^b	1.457 (8)		-C(4)B		1.300 (9)
-C(10)		1.535 (5)	C(5)B-C(4)B		1.334 (9)
			-C(6)B		1.332 (9)
O(1)-Cu(1)-O(1)^a	76.3 (1)	76.1 (1)	C(6)-C(7)-C(8)	115.0 (4)	109.1 (3)
O(1)^a-Cu(1)-O(2)^a	93.4 (1)	93.7 (1)	-C(9)	108.3 (3)	106.8 (3)
O(1)-Cu(1)-N(1)	94.2 (1)	94.3 (1)	-C(9)^b	108.3 (3)	
O(2)^a-Cu(1)-N(1)	96.1 (2)	95.8 (1)	-C(10)		113.1 (3)
Cu(1)-O(1)-Cu(1)^a	103.7 (1)	103.9 (1)	C(8)-C(7)-C(9)	109.2 (4)	109.9 (4)
C(4)-O(1)-Cu(1)^a	127.7 (3)	127.7 (2)	-C(9)^b	109.2 (4)	
-Cu(1)	128.7 (3)	128.5 (2)	-C(10)		108.5 (3)
Cu(1)^a-O(2)-C(6)	126.5 (3)	125.8 (2)	C(9)-C(7)-C(9)^b	106.4 (9)	
Cu(1)-N(1)-C(2)	123.9 (3)	123.6 (2)	-C(10)		109.4 (4)
-C(1)R	118.1 (3)	117.4 (2)	N(1)-C(1)R-C(2)R	120.3 (2)	120.8 (3)
C(2)-N(1)-C(1)R	118.1 (4)	118.9 (3)	-C(2)R^b	120.3 (2)	
N(1)-C(2)-C(1)	120.5 (4)	119.3 (3)	-C(6)R		119.6 (3)
-C(3)	124.7 (4)	124.5 (3)	C(2)R-C(1)R-C(2)R^b	119.3 (4)	
C(1)-C(2)-C(3)	114.8 (4)	116.3 (3)	-C(6)R		119.5 (3)
C(2)-C(3)-C(4)	128.2 (4)	129.3 (3)	C(1)R-C(2)R-C(3)R	120.4 (4)	120.6 (3)
C(3)-C(4)-O(1)	120.3 (4)	119.7 (3)	C(2)R-C(3)R-C(4)R	119.9 (4)	118.3 (3)
-C(5)	119.7 (4)	121.1 (3)	C(3)R-C(4)R-C(3)R^b	120.2 (5)	
O(1)-C(4)-C(5)	120.0 (4)	119.2 (3)	-C(5)R		122.3 (3)
C(4)-C(5)-C(6)	126.8 (4)	127.9 (3)	-N(2)R		118.8 (4)
C(5)-C(6)-O(2)	125.7 (4)	125.6 (3)	C(5)R-C(4)R-N(2)R		118.8 (4)
-C(7)	121.1 (4)	122.3 (3)	C(4)R-N(2)R-O(1)R		118.3 (4)
O(2)-C(6)-C(7)	113.2 (4)	112.0 (3)	-O(2)R		118.6 (4)
			O(1)R-N(2)R-O(2)R		123.1 (4)
			C(4)R-C(5)R-C(6)R		118.4 (3)
			C(5)R-C(6)R-C(1)R		120.8 (3)
			C(3)B^c-C(1)B-C(2)B	119.5 (7)	
			C(6)B-C(1)B-C(2)B		119.6 (7)
			C(1)B-C(2)B-C(3)B	121.1 (7)	119.6 (7)
			C(2)B-C(3)B-C(1)B^c	119.4 (7)	
			-C(4)B		121.0 (7)
			C(3)B-C(4)B-C(5)B		120.1 (6)
			C(4)B-C(5)B-C(6)B		119.7 (6)
			C(5)B-C(6)B-C(1)B		120.1 (7)

[a] Atom is located at $(-x, -y, -z)$ for $Cu_2(PAAan)_2\cdot C_6H_6$ and at $(^1/_2 - x, {}^1/_2 - y, 1 - z)$ for $Cu_2(PAApnan)_2\cdot 2C_6H_6$. [b] Atom is located at $(x, -y, z)$ for $Cu_2(PAAan)_2\cdot C_6H_6$. [c] Atom is located at $(-x, 1 - y, -z)$ for $Cu_2(PAAan)_2\cdot C_6H_6$;

Magnetic susceptibility measurements on the unrecrystallized microcrystals of $Cu_2(PAAan)_2$ and $Cu_2(PAApnan)_2$ and on the crystals $Cu_2(PAAan)_2\cdot C_6H_6$ and $Cu_2(PAApnan)_2\cdot 2C_6H_6$ proved that both compounds are diamagnetic at room temperature. This is consistent with a singlet ground-state–triplet excited-state separation of more than 850 cm^{-1}.

Discussion

The nature of axial interactions in Cu(II) complexes has been an area of continual interest from the standpoint of Jahn–Teller effects and reactivity at the axial positions. Numerous single-crystal X-ray structural studies have established the fact that, in general, the Cu(II) has at least one long bond to an axial ligand. Drago[10] has shown that interaction with an axial ligand is greatly influenced by the electronic effects of the ligands supplying the four primary donor atoms. For example, the Cu(II) in bis(hexafluoroacetylacetonato)copper(II) is apparently a considerably stronger Lewis acid than the Cu(II) in bis(acetylacetonato)copper(II). Our interest in axial ligation in binuclear Cu(II) complexes stems from a desire to understand the effect of various structural and electronic parameters on magnetic-exchange interactions.

The structures of the two binuclear Cu(II) complexes described herein differ from the previously reported bis(1,3,5-triketonato)dicopper(II) structures[3] in at least three important ways, all related to axial ligation. The first is a lack of a definitive axial ligand(s). The second is the near coplanarity of copper atoms, the donor atoms, and the ligand "backbone" carbon atoms. The third is the presence and position of the nonpolar solvent, benzene. The first two differences are related and bear upon the interpretation of the magnetic properties of this class of binuclear complexes. The third indicates a

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(10) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334.

unique interaction for metal complexes. This interaction is structurally similar to that found in organic π-molecular complexes.

Magnetic susceptibility measurements on $Cu_2(PAAan)_2{\cdot}C_6H_6$ and $Cu_2(PAApnan)_2{\cdot}2C_6H_6$ proved that both compounds are rigorously diamagnetic at room temperature, consistent with a singlet ground-state–triplet excited-state separation greater than 850 cm^{-1}. Since these compounds exhibit the strongest antiferromagnetic exchange yet observed in the dicopper(II) triketonates and the copper atoms are coplanar with the donor atoms, one can conclude that coplanarity is a condition for optimal antiferromagnetic exchange. Since the copper orbitals containing the unpaired electrons are in the plane of the donor atoms ($d_{x^2-y^2}$), coplanarity would be expected to result in the most efficient orbital overlap. The other structural feature considered to be of primary importance in determining the strength of the exchange is the Cu–O–Cu bridging angle, which is essentially constant throughout the entire series of bis(1,3,5-triketonato)dicopper(II) complexes at 103.4 ± 0.4°.[3] The other internal angle, O–Cu–O, is also relatively constant at about 76 ± 1°.[3]

It is obvious at this point that the magnetic exchange between Cu(II) ions in polynuclear complexes is quite sensitive to a number of structural parameters.[11] The simplicity of the coordination environment of the Cu(II) ions in the title compounds allows one to focus on the coplanarity as a contributor to strong antiferromagnetism. Although there are obvious electronic differences between $Cu_2(PAAan)_2$ and $Cu_2(PAApnan)_2$ and the rest of the 1,3,5-triketonates, it does seem clear that coplanarity in the compounds discussed herein vs. the usual 0.25-Å deviation from the ligand plane[3b] contributes to a strong antiferromagnetic exchange. While it is not possible to assess the effect of substituting an aniline-type nitrogen for a ketonic oxygen on the magnetic-exchange strength at this point, the structural effect on the coordination sphere is small and mainly reflected in the Cu–donor atom bond distances (Cu(1)–N(1) and Cu(1)–O(2)).

Certainly the most unusual aspect about the solid structure of these compounds is the formation of stacks in which benzene and complex molecules are interspersed in parallel planes. All features of the solid structures are consistent with the accepted definition of π-molecular complexes.[12] In both $C_6H_6{:}Cu_2(PAAan)_2$[13] and $(C_6H_6)_2{:}Cu_2(PAApnan)_2$,[13] the distance between the parallel benzene and complex planes is 3.26 Å. The commonly accepted range of interplanar distances between donor and acceptor molecules in π-molecular complexes is 3.20–3.35 Å,[14] the high end being the interplanar distance in graphite. The two π-molecular compounds are examples of the two most common types encountered, ADAD and DADDAD. For totally organic π-molecular complexes of these two types, the periodicity along the stacks is about 7 and 10.5 Å, respectively.[15] In excellent agreement with these values, the periodicity for $C_6H_6{:}Cu_2(PAAan)_2$ is 6.52 Å and for $(C_6H_6)_2{:}Cu_2(PAApnan)_2$ is 10.38 Å. The short interplanar distances and the nature of the stacking in the two compounds is good evidence for an interaction between the benzene, which is presumably a π-electron donor, and the binuclear complex acting as the acceptor.

The stoichiometry change from 1:1 to 2:1, benzene to complex, that accompanies the replacement of the aniline group for *p*-nitroaniline also argues strongly that there is an interaction between benzene and the complex more significant than simple packing forces. Introduction of the *p*-nitro group does not in itself affect the volume of space above and below the molecular plane and, therefore, could not be expected to change the stoichiometry so dramatically if the only consideration was crystal packing. However, introduction of the electron-withdrawing *p*-nitro group can be expected to increase the Lewis acidity of the copper ions. This increase in acceptor properties is consistent with the fact that $Cu_2(PAApnan)_2$ interacts independently with two benzene donor molecules, while $Cu_2(PAAan)_2$ shares two benzenes equally with two other complex molecules. Thus, the stoichiometry change accompanying the addition of the *p*-nitro groups is consistent with a π-molecular type interaction. The strongest indication that the metal ions play an active role in the interaction is the fact that the benzene molecules are located directly over the four-membered Cu_2O_2 ring in the center of the molecule.

In conclusion, $C_6H_6{:}Cu_2(PAAan)_2$ and $(C_6H_6)_2{:}Cu_2(PAApnan)_2$ appear to be the first examples of a new class of π-molecular compounds containing coordination complexes that interact with π-electron donors *at the metal site*. The rigorous coplanarity of the Cu(II) ions and the donor atoms, together with the complexes' room-temperature diamagnetism, demonstrates the importance of optimal orbital overlap in producing strong antiferromagnetic exchange.

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Registry No. H_2PAA, 85318-88-3; H_2PAAan, 85318-89-4; $Cu_2(PAAan)_2$, 85319-02-4; $Cu_2(PAApnan)_2$, 85319-03-5; $Cu_2(PAAan)_2{\cdot}C_6H_6$, 58354-03-6; $Cu_2(PAApnan)_2{\cdot}2C_6H_6$, 85354-04-7; H_2PAA, 66734-21-2; 4-nitroaniline, 100-01-6; aniline, 62-53-3.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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(11) Livermore, J. C.; Willett, R. D.; Gaura, R. M.; Landee, C. P. *Inorg. Chem.* **1982**, *21*, 1403 and references therein. Willett, R. D. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; American Chemical Society: Washington, DC, 1982; INOR 30.

(12) Herbstein, F. H. "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1971; Vol. 4, p 166.

(13) The formulas are written with the commonly used convention in which the donor molecule precedes the acceptor.

(14) Reference 12, p 244.

(15) Reference 12, pp 244–247.