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Synthesis, Magnetic and Spectroscopic Characterization of Copper(II) Toluate Complexes with Substituted Piperazines

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New copper(II) toluate complexes with the saturated heterocyclic bases [(L-L) having the tendency to coordinate through both 1 and 4 nitrogen atoms] 1-methylpiperazine, 1,4-dimethylpiperazine, 2,6-dimethylpiperazine and 1-phenylpiperazine have been prepared and characterized by physico-chemical and spectroscopic methods. All of the complexes were found to be antiferromagnetic with stoichiometries of the type $Cu(OOCR)_2(L\text{-}L)_n$ ($n = 1$ or 0.5, $R = 2$-, 3- or 4-$CH_3C_6H_4$) except $Cu(OOCC_6H_4CH_3\text{-}4)_2(L\text{-}L)$ (where L-L = 2,6-dimethylpiperazine), which is magnetically dilute. The spin exchange parameter, $-2J$, for two of the antiferromagnetic complexes has been evaluated from magnetic susceptibility measurements at different temperatures. Binuclear copper(II) acetate monohydrate-like structure for the antiferromagnetic complexes of 1:1 stoichiometry and polymeric structure of the type $Cu(OOCH)_2(dioxan)_{0.5}$ for the complexes of 1:0.5 stoichiometry have been proposed. The magnetically dilute complex has been assigned a polynuclear trans-pseudo-octahedral or polymeric square pyramidal structure.

Keywords Adducts, characterization, copper, magnetic, piperazines, spectroscopic, synthesis, toluate

INTRODUCTION

Copper(II) acetate forms both magnetically dilute and antiferromagnetic complexes with nitrogen and oxygen donor ligands (Doedens, 1976; Kato et al., 1964; Melnik, 1981a,b; Melnik, 1982; Oldham, 1968). The structure of the complexes depends upon factors such as the steric characteristics of the ligand, the stoichiometry of the complex, and reaction conditions (Bajju, 2002; Catterick and Thornton, 1977; MacDougall et al., 1976; Melnik, 1981; Valentine, et al., 1974). Oxygen donor organic ligands and pyridine-type nitrogen donors generally give antiferromagnetic complexes with copper(II) acetate (Bajju, 2002; Doedens, 1976; MacDougall, et al., 1976; Melnik, 1981; Melnik, 1982; Valentine et al., 1974), whereas saturated amine donors prefer to form magnetically dilute complexes (Kato et al., 1964; Melnik, 1981; Oldham, 1968; Stevens and Yoke, 1970). The influence of the steric and electronic characteristics of pyridine-type ligands on the structural and magnetic properties of their complexes with copper(II) acetate have been the subject of systematic investigations (Bajju 2002; Catterick and Thornton 1977; MacDougall et al., 1976; Valentine et al., 1974), but only a few reports exist on saturated heterocyclic bases. In the present study, the complexation properties of the diheterocyclic bases (L-L) (Figure 1*a*) 1-methylpiperazine (1-MePipz); 1,4-dimethylpiperazine (1,4-Me_2Pipz); 2,6-dimethylpiperazine (2,6-Me_2Pipz) and 1-phenylpiperazine (1-PhPipz) with copper(II) toluates [toluates = $OOCC_6H_4CH_3$-*n* where $n = 2$, 3 or 4 (Figure 1*b*)] have been undertaken. The interest in the present investigations was to see the role of pK_a of the parent carboxylic acid in structure determination and the effect of steric and electronic properties of the six-membered saturated diheterocyclic bases on the stoichiometry, magnetic behavior and structure of the complexes. An additional interest to the present studies was to see whether the heterocyclic bases, which in their free state exist in the chair conformation, coordinate to the metal ion in their chair or in the boat form.

EXPERIMENTAL

Starting Materials

Liquid heterocyclic bases such as 1-MePipz, 1,4-Me_2Pipz, 2,6-Me_2Pipz and 1-PhPipz (all from Fluka) were dried by refluxing and distilling over sodium hydroxide pellets before use. The liquids obtained after distillation were stored over sodium hydroxide beads. Acetone, *n*-hexane, solvent diethyl ether and petroleum ether (40–60 °C), all from BDH, and were purified by the usual methods.

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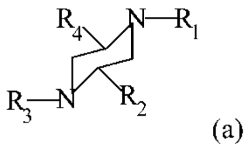
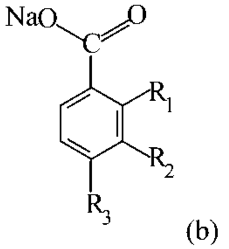


1-MePipz: $R_1 = R_2 = R_4 = H; R_3 = CH_3$
1,4-Me$_2$Pipz: $R_1 = R_3 = CH_3; R_2 = R_4 = H$
2,6-Me$_2$Pipz: $R_1 = R_3 = H; R_2 = R_4 = CH_3$
1-PhPipz: $R_1 = R_2 = R_4 = H; R_3 = C_6H_5$



$NaOOCC_6H_4CH_3$-2: $R_1 = CH_3; R_2 = R_3 = H$
$NaOOCC_6H_4CH_3$-3: $R_2 = CH_3; R_1 = R_3 = H$
$NaOOCC_6H_4CH_3$-4: $R_3 = CH_3; R_1 = R_2 = H$

FIG. 1. Structures of the ligands, (*a*) heterocyclic bases (L-L) and (*b*) sodium toluates.

Preparation of Copper(II) Toluates (*ortho-*, *meta-* and *para*)

The copper(II) toluates were synthesised by the method described earlier (Manhas et al., 2003).

Preparation of Complexes

Copper(II) toluate (1 g, 2.99 mmol), prepared by the method described earlier (Manhas et al., 2003), was suspended in diethyl ether (30 mL) in a round-bottomed flask. A solution of the stoichiometric amount (1.50 mmol or 2.99 mmol) of the heterocyclic base in the same solvent (15 mL) was added drop-wise after successive intervals of 10 min over a total period of about 2.5 h to the continuously stirred suspension of copper(II) toluate. Colored solutions, as indicated in Table 1, of the adducts were obtained as the solid copper(II) toluate dissolved. Solid adducts of the bases separated after the contents had been stirred for another two hours and then cooled. The separated product was filtered in a G_4 filtration unit, washed with acetone and diethyl ether, dried under vacuum and placed in a desiccator containing anhydrous calcium chloride.

Elemental Analyses and Physical Measurements

The metal content in the complexes was determined volumetrically by EDTA titration using xylenol orange as indicator. Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyzer, while nitrogen was determined by Kjeldahl's method in the departmental microanalytical laboratory. Infrared spectra of the copper(II) toluate (*ortho-*, *meta-* and *para-*) complexes with heterocyclic bases and their anhydrous sodium toluates were recorded as KBr pellets on a Pye Unicam SP3-300 infrared spectrophotometer in the 4000–200 cm^{-1} region. Electronic reflectance spectra of the complexes (either neat or diluted with an appropriate amount of $MgCO_3$) were recorded on a Unicam SP-700 UV-Visible spectrometer having a SP-735 diffuse reflectance attachment (50,000–4,000 cm^{-1}). The X-band EPR measurements (9.439–9.442 GHz) of powdered samples at room temperature were made on a JES-FE3XG electron paramagnetic resonance spectrometer. Room temperature magnetic susceptibilities of all the complexes were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. The magnetic susceptibility of the two complexes at 294, 160, 100 and 80 K were measured on a Par-155 vibrating sample magnetometer with a variable temperature cryostat. The measured susceptibilities were corrected for the diamagnetic susceptibility of the ligands. The correction for temperature was taken as 60×10^{-6} c.g.s. units per gram atom of copper(II) ions.

RESULTS AND DISCUSSION

Adducts of copper(II) toluates with substituted piperazines were obtained by reacting copper(II) toluates and piperazine in 1:0.5, 1:1 and 50% excess of stoichiometric amounts whereby the bases yield complexes only with the 1:1 and 1:0.5 stoichiometries (Eq. 3 and 4). Copper(II) toluates were prepared by reacting copper(II) sulfate with stoichiometric amounts of sodium salts of the corresponding toluic acids in a water-acetone mixture.

$$\begin{aligned} &HOOCC_6H_4CH_3\text{-}n + NaOH \\ &\quad \longrightarrow NaOOCC_6H_4CH_3\text{-}n + H_2O \end{aligned} \qquad [1]$$

$$\begin{aligned} &2(NaOOCC_6H_4CH_3\text{-}n) + CuSO_4 \cdot 5H_2O \\ &\quad \longrightarrow Cu(OOCC_6H_4CH_3\text{-}n)_2 + Na_2SO_4 + 5H_2O \end{aligned} \qquad [2]$$

$$\begin{aligned} &Cu(OOCC_6H_4CH_3\text{-}n)_2 + (\text{L-L}) \\ &\quad \longrightarrow Cu(OOCC_6H_4CH_3\text{-}n)_2(\text{L-L}) \end{aligned} \qquad [3]$$

$$\begin{aligned} &Cu(OOCC_6H_4CH_3\text{-}n)_2 + 0.5(\text{L-L}) \\ &\quad \longrightarrow Cu(OOCC_6H_4CH_3\text{-}n)_2(\text{L-L})_{0.5} \end{aligned} \qquad [4]$$

where $n = 2$, 3 or 4 and (L-L) = 1-MePipz; 1,4-Me$_2$Pipz; 2,6-Me$_2$Pipz and 1-PhPipz.

The complexes are insoluble in organic solvents and do not melt, but decompose above 185 °C. Chemical formulae based upon elemental analyses, colors and particulars of method of preparation of complexes are listed in Table 1.

TABLE 1

Elemental analysis (%). found (calcd.), colours and particulars of the method of preparation of the complexes

Compound (empirical formula) (formula weight)	Yield (%)	Elemental analysis, found (calcd.) (%)				Color	S.a. or excess[a]	Dec. p. (°C)
		Cu	C	H	N			
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)$	90	14.76	57.72	5.84	6.85	Pale	Excess	230
$(C_{21}H_{26}CuN_2O_4)$ (433.5)		(14.64)	(58.12)	(6.04)	(6.45)	blue		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)_{0.5}$	95	16.68	57.33	4.98	3.61	Pale	S.a.	225
$(C_{18.5}H_{20}CuNO_4)$ (383.5)		(16.55)	(57.88)	(5.25)	(3.65)	blue		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)$	90	14.53	58.48	5.95	6.21	Pale	Excess	200
$(C_{22}H_{28}CuN_2O_4)$ (447.5)		(14.18)	(58.98)	(6.30)	(6.25)	green		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)_{0.5}$	85	16.65	58.88	4.91	3.66	Pale	S.a.	210
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)	green		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$	75	14.17	58.53	5.80	6.68	Violet	Excess	190
$(C_{22}H_{28}CuN_2O_4)$ (447.5)		(14.18)	(58.98)	(6.30)	(6.25)			
$Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)_{0.5}$	80	16.24	58.84	5.68	4.01	Dirty	S.a.	200
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)	grey		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)$	80	12.71	62.79	5.31	5.25	Pale	S.a.	190
$(C_{26}H_{28}CuN_2O_4)$ (495.5)		(12.81)	(62.95)	(5.69)	(5.65)	green		
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)_{0.5}$	85	15.18	60.61	5.56	3.49	Sky	S.a.	200
$(C_{21}H_{21}CuNO_4)$ (414.5)		(15.31)	(60.79)	(5.10)	(3.38)	blue		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)$	90	14.71	58.02	5.87	6.19	Pale	Excess	220
$(C_{21}H_{26}CuN_2O_4)$ (433.5)		(14.64)	(58.12)	(6.04)	(6.45)	blue		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)_{0.5}$	95	16.18	57.62	4.76	3.66	Green	S.a.	230
$(C_{18.5}H_{20}CuNO_4)$ (383.5)		(16.55)	(57.88)	(5.25)	(3.65)			
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)$	80	14.61	58.58	5.93	5.98	Pale	S.a.	210
$(C_{22}H_{28}CuN_2O_4)$ (447.5)		(14.18)	(58.98)	(6.30)	(6.25)	green		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)_{0.5}$	85	16.06	58.88	4.89	3.92	Yellowish	S.a.	215
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)	green		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$	65	13.93	58.99	6.22	6.35	Blue	Excess	200
$(C_{22}H_{28}CuN_2O_4)$ (447.5)		(14.18)	(58.98)	(6.30)	(6.25)			
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)_{0.5}$	70	15.91	58.18	5.91	3.24	Pale	S.a.	195
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)	green		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)$	80	12.71	62.74	5.82	5.93	Pale	S.a.	205
$(C_{26}H_{28}CuN_2O_4)$ (495.5)		(12.81)	(62.95)	(5.69)	(5.65)	green		
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)_{0.5}$	85	15.39	60.29	5.55	3.12	Green	S.a.	200
$(C_{21}H_{21}CuNO_4)$ (414.5)		(15.31)	(60.79)	(5.10)	(3.38)			
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1,4\text{-}Me_2Pipz)_{0.5}$	80	16.34	58.04	5.89	3.83	Pale	Excess	220
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)	green		
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$	80	14.12	58.64	6.77	6.05	Pale	S.a.	190
$(C_{22}H_{28}CuN_2O_4)$ (447.5)		(14.18)	(58.98)	(6.30)	(6.25)	green		
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)_{0.5}$	70	16.52	58.47	5.91	3.59	Green	S.a.	190
$(C_{19}H_{21}CuNO_4)$ (390.5)		(16.26)	(58.38)	(5.41)	(3.58)			
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1\text{-}PhPipz)_{0.5}$	80	15.18	61.28	5.46	2.99	Blue	S.a.	190
$(C_{21}H_{21}CuNO_4)$ (414.5)		(15.31)	(60.79)	(5.10)	(3.38)			

[a] Indicates as to whether the heterocyclic base was taken in stoichiometric amount (S.a.) or in excess.

IR Spectra

Since both the acetate group and the heterocyclic base can coordinate to the metal ion in a bidentate or monodentate fashion, in principle, many structural arrangements are possible. In the absence of definitive structural data, two criteria are currently employed to determine the coordinating mode of acetate groups, viz.; (1) the 'Δ criterion' (Catterick and Thornton, 1977) is based upon the difference in the ν_a(OCO) and ν_s(OCO) values, and (2) the directions of shifts criterion (Manhas and Trikha, 1982), which depends upon the directions of the ν_a(OCO) and ν_s(OCO) shifts in the complexes compared to their values in sodium acetate. Of these, the latter criterion is considered to be more important. Examination of the positions and directions of the shifts of ν_a(OCO) and ν_s(OCO) of the carboxylate group in the complexes as compared to their positions in sodium toluates (Table 2) suggests a bridging bidentate mode of coordination of the carboxylate group for all of the complexes.

The band due to ν(N-H) in the complexes of the bases 1-MePipz, 2,6-Me_2Pipz and 1-PhPipz, appears at lower wave numbers relative to its position in the free bases, thus clearly indicating the coordination of the bases through the nitrogen atom of the N−H groups. The band due to the C−H stretching frequency of the $N-CH_3$ group in the complexes of the bases 1-MePipz and 1,4-Me_2Pipz either disappears or shifts to the higher energy region. In the case of disappearance, these bands probably shift to the higher energy region (2,900 cm^{-1}) and overlap with stretching vibrational bands of other C−H bonds of the complexes. This shift indicates that the nitrogen atom of the $>N-CH_3$ group no longer has a lone pair of electrons and it acquired a partial positive charge due to its coordination with the metal ion (Manhas and Trikha, 1978; Braunholtz et al., 1958; Manhas et al., 1979). However, in some complexes (Table 2) the absence of any noticeable shift of the bands due to ν(C−H) of $>N-CH_3$ excludes the possibility of coordination of the nitrogen atom of the $N-CH_3$ group (Manhas and Trikha, 1978; Braunholtz et al., 1958; Manhas et al., 1979). No new bands of low or medium intensity (characteristic of the boat configuration) appear in the region 1,500−700 cm^{-1}, thus indicating that the bases are coordinated in the same form as in the free state, i.e., in the chair form. The appearance of additional bands around 450 cm^{-1} and 310 cm^{-1} as compared to the infrared spectra of uncomplexed cupric carboxylate and the

TABLE 2
Some coordinatively diagnostic features of infrared spectra (cm^{-1}) of sodium salts of carboxylic acids, heterocyclic bases and their copper(II) complexes

Compound	ν(N-H)	ν(C−H) $N-CH_3$ or $N-C_6H_5$	ν_a(OCO)	ν_b(OCO)	ν(Cu−O)	ν(Cu−N)
4-$CH_3C_6H_4COO$ Na	—	—	1,545 s	1,406 vs	—	—
3-$CH_3C_6H_4COO$ Na	—	—	1,560 s	1,405 vs	—	—
2-$CH_3C_6H_4COO$ Na	—	—	1,515 s	1,403 vs	—	—
1-MePipz	3,280 m	2,680 m				
		2,820 m				
1,4-Me_2Pipz	—	2,680 m				
	—	2,840 m				
2,6-Me_2Pipz	3,265 m	—				
1-Phpipz	3,300 m	[a]				
$Cu(OOCC_6H_4CH_3\text{-}4)_2$(1-MePipz)	3,200 m	2,780 m	1,555 s	1,406 vs	452 m	290 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{1-MePipz})_{0.5}$	3,190 m	[a]	1,552 s	1,405 vs	450 m	300 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{1,4-Me}_2\text{Pipz})$	—	[a]	1,585 s	1,406 vs	446 m	295 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{1,4-Me}_2\text{Pipz})_{0.5}$	—	[a]	1,560 s	1,408 vs	455 m	305 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{2,6-Me}_2\text{Pipz})$	3,060 m	—	1,552 s	1,406 vs	415 m	280 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{2,6-Me}_2\text{Pipz})_{0.5}$	3,070 m	—	1,595 s	1,408 vs	422 m	295 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2$(1-PhPipz)	3,295 m	2,850 m	1,560 s	1,408 vs	450 m	305 s
$Cu(OOCC_6H_4CH_3\text{-}4)_2(\text{1-PhPipz})_{0.5}$	3,280 m	[a]	1,555 s	1,418 vs	435 m	305 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2$(1-MePipz)	3,125 m	2,780 m	1,575 s	1,420 vs	435 m	300 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{1-MePipz})_{0.5}$	3,280 s	[a]	1,575 s	1,410 vs	405 m	285 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{1,4-Me}_2\text{Pipz})$	—	[a]	1,572 s	1,410 vs	445 m	290 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{1,4-Me}_2\text{Pipz})_{0.5}$	—	[a]	1,580 s	1,405 vs	445 m	280 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{2,6-Me}_2\text{Pipz})$	3,130 m	—	1,560 s	1,405 vs	430 m	278 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{2,6-Me}_2\text{Pipz})_{0.5}$	3,260 m	—	1,570 s	1,415 vs	480 m	275 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2$(1-PhPipz)	3,280 m	2,840 m	1,570 s	1,390 vs	475 m	320 s
$Cu(OOCC_6H_4CH_3\text{-}3)_2(\text{1-PhPipz})_{0.5}$	3,210 m	[a]	1,572 s	1,420 vs	420 m	330 s
$Cu(OOCC_6H_4CH_3\text{-}2)_2(\text{1,4-Me}_2\text{Pipz})_{0.5}$	—	[a]	1,570 s	1,402 vs	450 m	285 s
$Cu(OOCC_6H_4CH_3\text{-}2)_2(\text{2,6-Me}_2\text{Pipz})$	3,245 m	—	1,565 s	1,430 vs	460 m	310 s
$Cu(OOCC_6H_4CH_3\text{-}2)_2(\text{2,6-Me}_2\text{Pipz})_{0.5}$	3,230 m	—	1,565 s	1,405 vs	475 m	305 s
$Cu(OOCC_6H_4CH_3\text{-}2)_2(\text{1-PhPipz})_{0.5}$	3,270 m	[a]	1,565 s	1,420 vs	405 m	295 s

[a] means absorbance is not observed clearly.

free bases have tentatively been assigned to ν(Cu–O) and ν(Cu–N) modes of vibrations, respectively (Manhas and Trikha, 1978; Marcotrigiano et al., 1972; Battaglia, 1980; Manhas and Dhindsa, 1989).

Electronic Reflectance Spectral Studies

The complex $Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$ shows two bands around 16,000 and 20,000 cm^{-1} in its diffuse electronic reflectance spectrum. The appearance of these bands indicates tetragonal distortion (D_{4h} symmetry) of the octahedral field for the copper(II) ion in this complex. The lower and higher energy bands can be assigned to $^2B_{2g} \leftarrow {}^2B_{1g}(d_{xy} \rightarrow d_{x^2-y^2})$ and $^2E_g \leftarrow {}^2B_{1g}$ $(d_{xz}, d_{yz} \rightarrow d_{x^2-y^2})$ ligand field transitions (Hathaway and Billing, 1970). Here the difference between the two 'd-d' transitions is apparently larger. The splitting into two of the electronic spectral band (due to the $^2T_{2g} \leftarrow {}^2E_g$ transition), expected for a regular octahedral copper(II) complex, is not surprising. Most copper(II) complexes are distorted due to the Jahn-Teller effect. Moreover, in the present case the complexes are bound to be distorted due to the large difference in the ligand field strengths of carboxylate ligands and the bases. Another band at 33,335 cm^{-1} is probably due to the ligand → metal ($2p_\pi$ (donor oxygen atom) → $(d_{x^2-y^2})^*$) charge transfer transition (Dubicki, 1972; Dubicki and Martin, 1966). All other complexes show a broad band in the region 12,500-14,925 cm^{-1} in their diffuse electronic reflectance spectra (Table 3). It is a composite band (band I) and is considered to contain bands due to the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ electronic transitions for copper(II) ion in tetragonal environments. The band II, which appears as a shoulder at about $32{,}000 - 37{,}000\,cm^{-1}$, is assigned to the charge transfer transition $2p_\pi(O) \rightarrow (d_{x^2-y^2})^*$ (Dubicki, 1972; Dubicki and Martin, 1966).

EPR Studies

The X-band EPR curve of powdered material for the magnetically dilute copper(II) complex $Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$ has been obtained at room temperature and is consistent with the axial symmetry of the complex. The magnitude of $g_\parallel$ (2.2866) and $g_\perp$ (2.0916) obtained from the EPR spectrum for this complex is consistent ($g_\parallel > g_\perp > 2.04$) with an elongated type structure, and hence $d_{x^2-y^2}$ as the higher energy orbital. This agrees with the results obtained from electronic absorption studies (Attanasio et al., 1974; Hathaway and Billing, 1970). The observed range of $g_\parallel$ is in

TABLE 3
Electronic reflectance spectral data (cm^{-1}) and room temperature μ_{eff} values of the magnetically dilute and antiferromagnetic copper(II) toluates with substituted piperazines

Compound	Absorption I d-d transitions	Absorption II (ligand → metal charge transfer transitions)	μ_{eff} (B.M.)
$Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$	16,000 20,000	33,335	1.870
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)$	13,700		1.372
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)_{0.5}$	13,795	36,365	1.420
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)$	13,160	34,485	1.404
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)_{0.5}$	12,500	33,335	1.420
$Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)_{0.5}$	14,925	35,715	1.460
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)$	13,605	33,335	1.368
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)_{0.5}$	14,285	33,900	1.347
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)$	13,985	35,090	1.398
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)_{0.5}$	13,795	35,715	1.451
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)$	12,985	35,715	1.295
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)_{0.5}$	13,515	37,035	1.360
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$	13,700	30,770	1.546
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)_{0.5}$	13,795	35,715	1.411
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)$	13,700	37,035	1.470
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)_{0.5}$	13,515	35,715	1.482
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1,4\text{-}Me_2Pipz)_{0.5}$	13,160	37,035	1.472
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$	13,335	37,035	1.414
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)_{0.5}$	13,890	35,715	1.420
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1\text{-}PhPipz)_{0.5}$	14,085	35,090	1.339

conformity with the CuO_4N_2 chromophore of the complex (Attanasio et al., 1974). The orbital reduction factors $K_{\|}^2 = 0.6855$ and $K_{\perp}^2 = 1.0764$ ($K_{\|}^2 < K_{\perp}^2$ suggests that in-plane π-bonding may be dominating. These values are comparable to other copper(II) systems (actually $K_{\|}^2 = \lambda_{\|}/\lambda_0$ and $K_{\perp}^2 = \lambda_{\|}/\lambda_0$ where λ_0 is spin-orbit coupling constant for free copper(II) ion and $\lambda_{\|}$ and $\lambda_{\perp}$ are effectively reduced spin-orbit coupling constants due to covalency in the complexes Hathaway and Billing, 1970). The calculated value of $G = 3.1825$, which is <4.0, shows that significant exchange coupling is present and the misalignment is appreciable.

The X-band EPR spectra at 300 K for powdered samples of antiferromagnetic complexes in the present discussion contain absorption lines at field strengths of 600 (H_{z1}), 4700 ($H_{\perp}$), and 6100G (H_{z2}), which are characteristic features of axially symmetric binuclear copper(II) species and correspond to the spin triplet state ($S = 1$) with $D > h\nu$ and $E = 0$ (Smith and Pilbrow, 1974) (Table 4). The range of $g_{\|}$ or g_z (2.34–2.51), $g_{\perp}$ (2.10–2.16) and D (0.34–0.40 cm^{-1}) evaluated from the EPR spectra are comparable with the earlier reported values for binuclear copper(II) carboxylate complexes (Catterick and Thornton, 1977; Jotham et al., 1972; Melnik, 1981; Melnik, 1982). However, in addition to the above mentioned absorptions, an absorption line around 3200 G is also observed. This line has been attributed to the magnetically dilute copper(II) impurity which is commonly present in copper(II) arylcarboxylate complexes (Newton et al., 1980; Thompson et al., 1971; Wasson et al., 1968).

Magnetic Susceptibility Studies

The room temperature magnetic moment for the complex $Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$ is 1.87 B.M., i.e., greater than the spin-only value for one unpaired electron (d^9 system), indicating the complex to be magnetically dilute while all the other complexes have μ_{eff} values in the 1.34–1.54 range (Table 3), which is similar to the values reported earlier for antiferromagnetic dinuclear or polynuclear complexes where carboxylate groups bridge between two metal ions (Table 5) (Catterick and Thornton 1977; Doedens 1976; Melnik 1981a, b; Melnik 1982).

The $Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$ and $Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$ complexes have been characterized by magnetic susceptibility measurements at 294, 160, 100 and 80 K. The magnetic moments for the two complexes decrease with a decrease of temperature, while the magnetic susceptibility of the first complex increases and that of the second complex decreases with a decrease of temperature. The increase of the magnetic susceptibility with decreasing temperature for $Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$ suggests that the complex either has a spin-exchange parameter ($-2J$) considerably smaller than the other complex or it has a much higher proportion of the magnetically dilute impurity, which is commonly found in antiferromagnetic complexes. Hence, the following modified equation, based upon Bleaney and Bower's model (Bleaney and Bowers, 1952) which takes into consideration the presence of a paramagnetic impurity, was employed to evaluate the value of $-2J$ from magnetic

TABLE 4
Electron paramagnetic resonance spectral parameters of antiferromagnetic complexes

Compound	$g_{\perp}$	$g_{\|}$	g_{av}	$\|D\|(cm^{-1})$
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)$	2.0976	2.4529	2.2160	0.3722
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}MePipz)_{0.5}$	2.1357	2.5099	2.2604	0.3706
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)$	2.1087	2.4529	2.2234	0.3722
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1,4\text{-}Me_2Pipz)_{0.5}$	2.1216	2.4983	2.2472	0.3733
$Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)_{0.5}$	2.1382	2.4529	2.2431	0.3722
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)$	2.0957	2.4485	2.2133	0.3710
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-}PhPipz)_{0.5}$	2.1607	2.3463	2.2226	0.3423
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)$	2.0976	2.4529	2.2160	0.3722
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}MePipz)_{0.5}$	2.1014	2.4416	2.2148	0.3741
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)$	2.1249	2.4418	2.2305	0.3976
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1,4\text{-}Me_2Pipz)_{0.5}$	2.1391	2.4983	2.2588	0.3966
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$	2.1024	2.4641	2.2230	0.3754
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)_{0.5}$	2.1018	2.4527	2.2188	0.3751
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)$	2.1188	2.4202	2.2193	0.3743
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-}PhPipz)_{0.5}$	2.1119	2.4757	2.2332	0.3786
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1,4\text{-}Me_2Pipz)_{0.5}$	2.1311	2.4757	2.2460	0.4017
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$	2.1266	2.4754	2.2429	0.3988
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)_{0.5}$	2.1244	2.4866	2.2451	0.4049
$Cu(OOCC_6H_4CH_3\text{-}2)_2(1\text{-}PhPipz)_{0.5}$	2.1135	2.4485	2.2252	0.371

TABLE 5

Magnetic susceptibility ($\chi^{1}_{Cu} \times 10^{6}$) (c.g.s units) data and values of spin exchange parameter ($-2J$) (cm^{-1}) of antiferromagnetic complexes and pK_a of axial ligand and carboxylic acid

Compound	Diamagnetic correction ($\times 10^6$)	$\chi^{1}_{Cu} \times 10^6 = [(\chi^{corr}{}_{Cu} - N_\alpha) \times 10^6]$				Carboxylic acid pK_a	Axial ligand pK_a	$-2J$
		294 K	160 K	100 K	80 K			
$Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$	254	1,017	1,078	1,108	1,108	4.252	$pK_{a1} = 9.570$ $pK_{a2} = 5.400$	274
$Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$	254	848	652	522	456	3.870	$pK_{a1} = 9.570$ $pK_{a2} = 5.400$	315

susceptibility data at different temperatures (Thompson et al., 1971; Newton et al., 1980).

$$\ln\left[\frac{Ng^{-2}\beta^{2}(1-x)}{kT(\chi Cu - 0.43x/T - N_\alpha)} - 3\right] = -\frac{2J}{kT}$$

$$\text{or} \quad \ln(F-3) = -\frac{2J}{kT} \qquad [5]$$

The unknown quantities in this expression on the left hand side were assumed as follows: the value of ($\bar{g} = 2.17$ normally found for copper(II) alkanoates and the value of N_α assumed to be constant at 60×10^{-6} c.g.s units (Jotham et al., 1972). The value of x, the mole fraction of paramagnetic impurity, was chosen to give the best fit with the above equation. Values of $-2J$ equal to 274 and 315 cm^{-1} for the $Cu(OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-}Me_2Pipz)$ and $Cu(OOCC_6H_4CH_3\text{-}2)_2(2,6\text{-}Me_2Pipz)$ complexes, respectively, were obtained from the slopes (2J/K) of the plots of ln (F-3) versus 1/T. The former complex was found to have a spin-exchange parameter ($-2J$), which is considerably smaller than that of the other complex. The range of values for $-2J$ of the present complexes with axial ligands having high donor ability (saturated amines) and is comparable to other aromatic nitrogen donor axial ligands (pyridine or quinoline, etc.) with less donor ability. The electronic nature of the axial ligand in the two complexes being kept the same, the large difference in the values of $-2J$ and their order of magnitude show a direct relationship with the pK_a values and, hence, the donor strengths of the parent *ortho*- and *meta*-toluic acids. *Ortho*-toluate with a lower pK_a value of its acid and higher acid strength (*ortho* effect) as compared to that of *meta*-toluate (Table 3) acts as a better donor. This results in the greater energy separation between the lower lying singlet and higher lying triplet energy states and, hence, a higher value of $-2J$ in its copper(II) complex. This is in conformity with the earlier existing results of Jotham et al. (Jotham et al., 1972) where it has been stated that $-2J$ increases as either the terminal ligands or the bridging ligands become better donors.

On the basis of the spectroscopic data, the complex $Cu(OOCC_6H_4CH_3\text{-}4)_2$ (2,6-Me_2Pipz) may have the structure shown in Figure 2*a* or 2*b* where the carboxylate ligand behaves as a bridging bidentate group. The structure in Figure 2*a* is polynuclear *trans*-pseudo-octahedral. Here the carboxylate group and the base L-L both act as bridging bidentate ligands, while Figure 2*b* shows that the carboxylate group acts as a bidentate ligand and the base L-L acts as a unidentate ligand (while taking the axial position) to give a polynuclear square pyramidal structure to the complex. Although in these

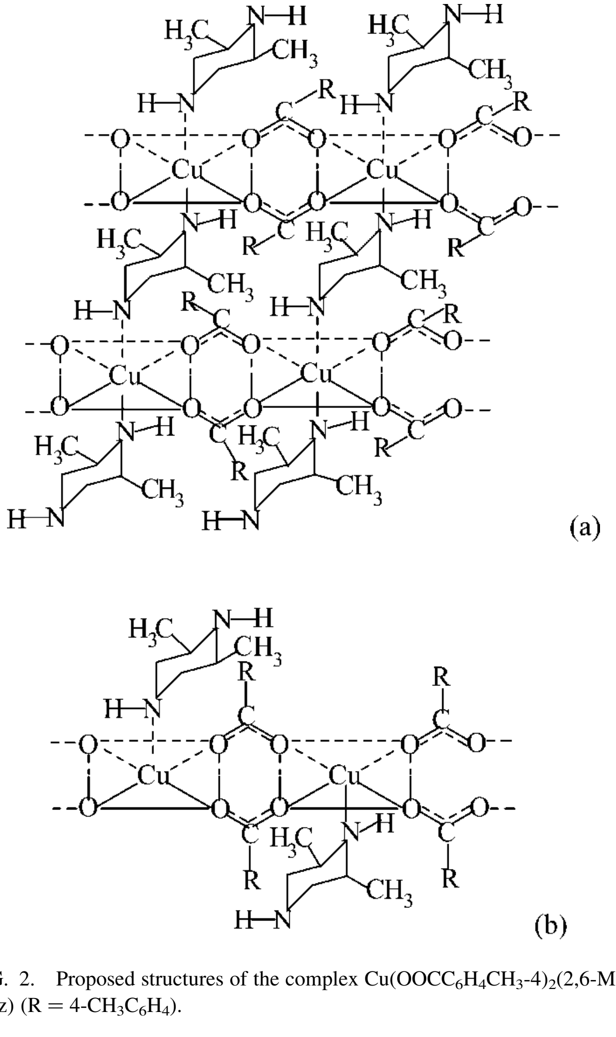
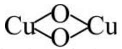


FIG. 2. Proposed structures of the complex $Cu(OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-}Me_2Pipz)$ ($R = 4\text{-}CH_3C_6H_4$).

structures there are two bridging carboxylate groups, there is very little interaction of the unpaired electrons on the two interacting copper ions via the intermediate carboxylate groups. This is in contrast to the copper(II) acetate monohydrate structure in which d_{xy} orbitals of copper ion interact with π orbitals of oxygens and the superexchange mechanism is made possible since the significant mixing of the magnetically important sigma-bonding ($d_{x^2-y^2}$) wave functions into π-bonding (d_{xy}) orbitals enables the delocalized π orbital system of bridging groups to become available. However, in the above-mentioned case, this type of mixing has to be very small as the energy difference between d_{xz}, d_{yz} and $d_{x^2-y^2}$ orbitals is much greater than that between d_{xz} and $d_{x^2-y^2}$. This conclusion is corroborated by the fact that in some Cu–O–Cu and  and bridged complexes where d_{xy} and d_{xz}, d_{yz} orbitals of the copper atoms are the π-interacting orbital(s) in the bridge, the magnetic exchange does not occur (Carlisle and Hatfield, 1970; Gruber et al., 1968; Hall and Waters, 1960; Hatfield, 1970; Hatfield, 1972; Lewis and Walton, 1966; Villa et al., 1970; Villa and Hatfield, 1970; Villa and Hatfield, 1971). For the antiferromagnetic complexes, a copper(II) acetate monohydrate-like binuclear structure (De Meester et al., 1973) may be assigned to the complexes of the type $Cu(OOCR)_2(L\text{-}L)$. A polymeric structure similar to $Cu(OOCH)_2(dioxan)_{0.5}$ (Figure 3) with carboxylate groups acting as bridging bidentate between two copper ions and the heterocyclic base (L-L) joining the two bridging units through copper atoms may be assigned to all the other antiferromagnetic complexes of the type $Cu(OOC_6H_4CH_3\text{-}n)_2(L\text{-}L)_{0.5}$.

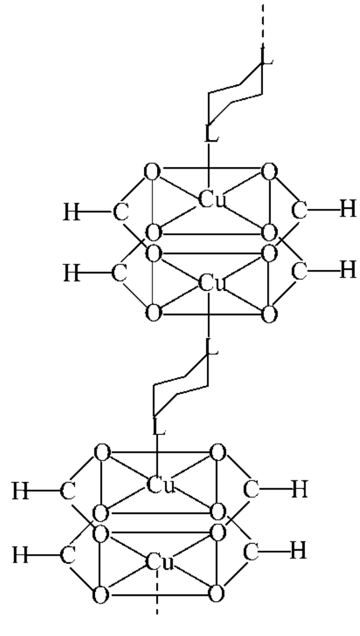


FIG. 3. Proposed structure for complexes of the type $Cu(OOC_6H_4CH_3\text{-}n)_2(L\text{-}L)_{0.5}$.

Overall, if we compare the room temperature μ_{eff} values for the whole series of complexes we are unable to make any convincing relationship with electronic and steric effects of the carboxylate as well as that of the heterocyclic secondary amine ligands. However, the steric hindrance of the amine ligands plays an important role in determining the stoichiometry, structure, and, hence, the magnetic properties (magnetically dilute and antiferromagnetic character) of the complexes. Though the pK_a of 4-toluic acid (4.360) is comparatively larger than that of 2-toluic acid (3.870) and 3-toluic acid (4.257), the smaller steric hindrance of the methyl group at the 4-position on the aryl ring in comparison to that of 2- and 3-toluic acids, appears to favor the formation of a magnetically dilute complex only with the base 2,6-Me_2Pipz, while all other bases yield antiferromagnetic complexes.

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