and it seems reasonable to assign the 303-cm^{-1} band to the stretching mode of the equatorial chloride cis to the iodide. The geometries of the chloride complexes indicate that oxidative addition reactions have produced trans products, that the rearrangement of ligands in the original complexes has not occurred (although one case of substitution was observed), and that the products are not necessarily the thermodynamically stable ones (since two pairs of isomers, $Pt(phen)Cl_2Br_2$, $Pt(phen)Br_2Cl_2$ and $Pt(phen)Cl_3I$, $Pt(phen)ICl_3$, were obtained).

The infrared spectra presented a more complicated aspect in the Pt–Br stretching region, 200–300 cm^{-1}. All of the complexes absorbed in this range. Inspection of the spectra revealed that bromide-containing compounds have some absorptions at frequencies where compounds not containing bromide did not absorb. $Pt(phen)Br_2$ and its derivatives had absorptions at 213–215, 245–249, and 260–265 cm^{-1}, the sole exception being $Pt(phen)Br_2$, for which the intermediate frequency was absent. Noting the parallel with the equatorial chloride vibrations 100 cm^{-1} higher, we expect the third absorption in the platinum(II) compound should lie near 238 cm^{-1}. In fact the strongest absorption in the spectrum of the compound lies at 239 cm^{-1}.

Compounds with axial bromide(s) absorbed at 201–210 and 251–253 cm^{-1}. If a trans effect operates in these compounds, their scarcity and the complexity of the spectra would make finding an absorption of variable frequency very difficult. The Pt–I stretching frequencies lie below 200 cm^{-1}, outside the capability of our spectrophotometer.

Registry No. $Pt(phen)Cl_2$, 18432-95-6; $Pt(phen)Br_2$, 42847-12-1; $Pt(phen)I_2$, 42847-13-2; $Pt(phen)Cl_4$, 17030-27-2; $Pt(phen)Br_2Cl_2$, 53432-67-0; $Pt(phen)Cl_2Br_2$, 53495-30-0; $Pt(phen)Br_4$, 53432-68-1; $Pt(phen)Cl_2(I_3)_2$, 53432-69-2; $Pt(phen)Br_2I(I_3)$, 53432-55-6; $Pt(phen)I_4$, 53432-56-7; $Pt(phen)I_3(I_3)$, 53432-57-8; $Pt(phen)Br_3Cl$, 53432-58-9; $Pt(phen)Br_2ICl$, 53432-59-0; $Pt(phen)Cl_3I$, 53432-60-3; $Pt(phen)I_3CN$, 53432-61-4; $Pt(phen)Cl_2(SCN)_2$, 53432-62-5; $Pt(phen)Br_2(SCN)_2$, 53466-61-8; $Pt(phen)ICl_3$, 53495-29-7; $Pt(phen)I_3Cl$, 53432-63-6; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; ICl, 7790-99-0; ICN, 506-78-5; $(SCN)_2$, 505-14-6; NOCl, 2696-92-6.

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Magnetic Exchange in Copper(II) Complexes of 7-Azaindole

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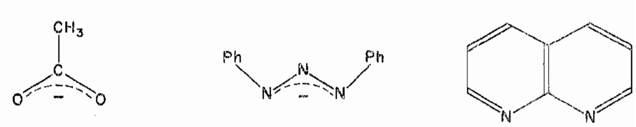
The ligand 7-azaindole (denoted by LH) has been found to form a variety of complexes with divalent copper. These complexes are formulated as $Cu(CH_3CO_2)_2{\cdot}LH$, $Cu(CH_3CO_2)(L){\cdot}LH$, $Cu(CH_3CO_2)(L){\cdot}py$, and $CuL_2{\cdot}2DMSO$. Variable-temperature magnetic susceptibility measurements indicate that substantial pairwise antiferromagnetic exchange between the copper atoms occurs in each case. Various other physical measurements including infrared, electronic, mass, and esr spectroscopy have been employed in the characterization of the complexes. A discussion of the probable molecular structures of the complexes is given. It is proposed that deprotonated 7-azaindole bridges two copper atoms in a syn,syn configuration. The possibility of a superexchange pathway involving triatomic deprotonated 7-azaindole bridges between two copper atoms is also considered.

Introduction

Nonlinear triatomic bidentate groups can function either as simple chelates or as binucleating ligands. The bridging potentialities of carboxylate anions, *e.g.*, acetate (**1**) were originally classified[2] in terms of syn,syn, anti,anti, or anti,syn conformations of OCO, the syn,syn mode being the basis of the binuclear copper(II) acetate structure.[3] The anion of 1,3-diphenyltriazene (**2**) provided the first examples[2,4] of binuclear metal complexes based on the syn,syn bridging by the triatomic NNN group and confirmatory X-ray structural evidence[5] is now available for the $Ni_2(dpt)_4$, $Pd_2(dpt)_4$, and $Cu_2(dpt)_4$ dimers (dpt denotes the 1,3-diphenyltriazenido anion).



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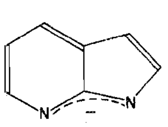
An investigation of the bridging potential of the triatomic NCN group represents a natural extension of these investigations. Initially, the neutral 1,8-naphthyridine (**3**) was studied in the hope that the ligating power of pyridine would enable the isolation of a more extended range of transition metal dimers. In the event, evidence for dimeric cations of the type $[M_2(1,8\text{-naphthyridine})_4]^{4+}$ has not emerged, either from our own studies[6] or from the extensive work of Hendricker[7] with this ligand. Accordingly, we initiated a study of the transition metal complexes of 7-azaindole (denoted by LH) with the intention of retaining the bridging NCN group but in an anionic (**4**) rather than a neutral (**5**) form. At this stage, considerable attention was focused on the bridging capabilities of a closely related system containing the NCN group, *viz.*, adenine (denoted by AdH), **6**. Sletten[8] has demonstrated by



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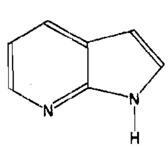

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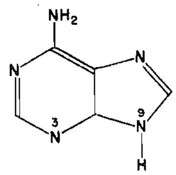

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X-ray methods that the complex $Cu(Ad)_2{\cdot}4H_2O$ is dimeric with the copper(II) acetate monohydrate structure. More recently, it has been established that neutral adenine functions as a syn,syn bidentate bridge (*via* N3 and N9) in the copper(II) compounds $[Cu_2(AdH)_4(H_2O)_2](ClO_4)_4{\cdot}2H_2O$[9] and $[Cu_2(AdH)_4Cl_2]Cl_2{\cdot}6H_2O$.[10] Protonated adenine has also been observed to function as a syn,syn bridge, *viz.*, in $[Cu_3(AdH_2)_2Cl_8]{\cdot}4H_2O$.[11] In contrast, the nitrogen atom N9 alone is coordinated to copper in the complex $[Cu_2(AdH)_2Br_2]Br_2$.[12]

The synthesis of these dimers is important for studying by magnetic and spectroscopic techniques the nature of the spin–spin interactions which occur intramolecularly between the metal atoms. These are relatively strong and lead to diamagnetism for the NNN-bridged $Cu_2(dpt)_4$. However, the low-lying triplet state is thermally accessible for the OCO-bridged $Cu(CH_3CO_2)_2{\cdot}H_2O$[13] and the NCN-bridged $Cu(Ad)_2{\cdot}4H_2O$,[14] and temperature-dependent magnetic moments are observed.

We have already reported[15] the existence of a dimeric nickel(II) complex of 7-azaindole for which we propose the bridging of two metal atoms by four anionic 7-azaindole ligands. This paper describes the chemistry of four copper(II) complexes which contain 7-azaindole coordinated either as the neutral molecule or in the deprotonated form. In particular, the temperature dependence of the magnetic moment of each complex suggests the existence of substantial antiferromagnetic exchange between pairs of divalent copper atoms.

Experimental Section

(a) $Cu(CH_3CO_2)_2{\cdot}LH$. $Cu(CH_3CO_2)_2{\cdot}H_2O$ (2.00 g) and 7-azaindole (0.59 g) were dissolved in 200 ml of methanol. The solution was heated and evaporated slowly. A light green crystalline material gradually precipitated from solution. The product was filtered, washed with methanol, and dried under vacuum. *Anal.* Calcd for $CuC_{11}H_{12}N_2O_4$: Cu, 21.19; C, 44.06; H, 4.04; N, 9.35. Found: Cu, 21.0; C, 44.34; H, 4.21; N, 9.27.

(b) $Cu(CH_3CO_2)(L){\cdot}LH$. Copper(II) acetate monohydrate (0.67 g) and 7-azaindole (2.00 g) were dissolved in approximately 40 ml of tetrahydrofuran. The green solution so formed was refluxed for 1 hr. Small dark green crystals were observed to form on the sides of the reflux vessel. The solution was cooled and the crystals were filtered, washed with tetrahydrofuran, and dried under reduced pressure. *Anal.* Calcd for $CuC_{16}H_{14}N_4O_2$: Cu, 17.75; C, 53.70; H, 3.94; N, 15.66. Found: Cu, 17.9; C, 53.84; H, 4.05; N, 15.45.

(c) $Cu(CH_3CO_2)(L){\cdot}py$. $Cu(CH_3CO_2)(L){\cdot}LH$ was dissolved in pyridine and the solution was warmed. Petroleum ether (bp 60–80°) was slowly added with stirring to precipitate the complex. The dark green polycrystalline material so obtained was washed with petroleum ether and dried under reduced pressure. *Anal.* Calcd for $CuC_{14}H_{13}N_3O_2$: Cu, 19.94; C, 52.73; H, 4.11; N, 13.18. Found: Cu, 20.1; C, 52.62; H, 4.12; N, 13.03.

(d) $CuL_2{\cdot}2DMSO$ (and $CuL_2{\cdot}2DMF$). $Cu(CH_3CO_2)_2{\cdot}H_2O$ (0.60 g) and 7-azaindole (0.71 g) were dissolved in 80 ml of warm DMSO and the solution was filtered. To this solution was added a methanolic solution of KOH (0.34 g in 5 ml). The resulting solution was swirled and filtered. On standing, small brown crystals separated from solution. These were filtered, washed sparingly with a DMSO–methanol mixture, and dried under vacuum for 12 hr. *Anal.* Calcd for $CuC_{18}H_{22}N_4S_2O_2$: Cu, 13.99; C, 47.61; H, 4.88; N, 12.34; S, 14.12. Found: Cu, 13.7; C, 47.32; H, 4.72; N, 12.00; S, 14.1.

When DMF was used in place of DMSO in the above procedure, a compound of formula $CuL_2{\cdot}2DMF$ was obtained. *Anal.* Calcd for $CuC_{20}H_{24}N_6O_2$: Cu, 14.32; C, 54.10; H, 5.45; N, 18.93. Found: Cu, 14.6; C, 54.08; H, 5.39; N, 18.77.

It is noted that green-black crystalline compounds, which analyze as $Cu(OCH_3)(L){\cdot}{}^1/_2DMSO$ and $Cu(OCH_3)(L){\cdot}{}^1/_2DMF$, were obtained by altering the methanol content of the DMSO–methanol (or DMF–methanol) solvent mixture to about 50:50 v/v in the above procedure. Interestingly, the compounds are effectively diamagnetic at room temperature, but they will not be further discussed in this work because their characterization is still incomplete.

Infrared Spectra. The infrared spectra were recorded in the region of 4000–250 cm^{-1}, a Perkin-Elmer 421 spectrophotometer being used. Samples were mounted in potassium bromide disks and in hexachlorobutadiene mulls between NaCl plates.

Electronic Spectra. Diffuse-reflectance spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer. Transmission spectra were measured in chloroform on a Hitachi EPS-3T spectrophotometer.

Electron Spin Resonance Spectra. Measurements were made on a Varian 4502 spectrometer operating at X-band frequency.

Magnetic Measurements. Magnetic susceptibilities were measured on a Gouy balance calibrated with $Hg[Co(NCS)_4]$. The field strength was 7600 G.

Mass Spectra. The spectra were recorded at 70 eV on a CH7 instrument. The source probe temperatures were 150° for $Cu(CH_3CO_2)(L){\cdot}LH$ and $Cu(CH_3CO_2)(L){\cdot}py$ and 230° for $CuL_2{\cdot}2DMSO$.

Analyses. All analyses were performed by the Australian Microanalytical Service, Melbourne, Australia.

Results and Discussion

We have found that a number of compounds are obtainable when solutions of copper(II) acetate monohydrate (CAM) and 7-azaindole are added together. Each compound has been prepared in an analytically pure form by suitable modification of the reaction conditions. Our initial intention was to prepare the inner complex Cu_2L_4 by mixing solutions of the ligand and CAM; *cf.* $Cu_2(dpt)_4$.[2] However, when 7-azaindole and an excess of CAM reacted in methanol, the light green crystalline complex $Cu(CH_3CO_2)_2{\cdot}LH$ was precipitated. Addition of CAM and excess 7-azaindole in solvent THF yielded dark green crystals of a compound which we have formulated as $Cu(CH_3CO_2)(L){\cdot}LH$. Recrystallization of this material from pyridine produced the pyridine analog $Cu(CH_3CO_2)(L){\cdot}py$.

The NH proton of 7-azaindole is not easily removed[16] and it is necessary to employ more basic conditions to prepare an inner complex of the form CuL_2. This was achieved by dissolving the correct stoichiometric proportions of CAM and 7-azaindole in DMSO (or DMF) and adding the required amount of KOH dissolved in a minimum amount of methanol. On standing, brown crystals of $CuL_2{\cdot}2DMSO$ (or $CuL_2{\cdot}2DMF$) were deposited from solution. In most respects, the physicochemical properties of $CuL_2{\cdot}2DMSO$ and $CuL_2{\cdot}2DMF$ are very similar. Therefore only one of the compounds (the former) is reported in detail.

Magnetic Properties. The magnetic susceptibilities of the complexes were recorded over the temperature range 85–370°K (see Table I). The calculated values of magnetic susceptibility and magnetic moment were obtained using the Bleaney and Bowers equation[17]

$$\chi_M - N\alpha = \frac{Ng^2\beta^2}{3kT}\,[1 + {}^1/_3 e^{-2J/kT}]^{-1}$$

where χ_M is the magnetic susceptibility (corrected for ligand diamagnetism) per mole of copper atoms.

In each case, the temperature dependence of the susceptibility is typical of an antiferromagnetically coupled pair of copper(II) atoms, giving an S = 0 ground state, with an S =

Table I. Magnetic Properties

T, °K	$10^6(\chi_M - N\alpha)$,[a] cm³ mol⁻¹ Obsd	Calcd[e]	μ_{eff},[c] BM Obsd	Calcd
$Cu(CH_3CO_2)_2$·LH (140 × 10^{-6} cm³ mol⁻¹)[b]				
92	119	125	0.30	0.30
101	191	175	0.39	0.38
120	314	294	0.55	0.53
152	494	482	0.77	0.77
174	596	584	0.91	0.90
205	668	680	1.05	1.06
237	728	733	1.17	1.18
261	750	752	1.25	1.25
287	754	758	1.32	1.32
321	742	751	1.38	1.39
342	732	740	1.41	1.42
368	715	724	1.45	1.46
$Cu(CH_3CO_2)(L)$·LH (176 × 10^{-6} cm³ mol⁻¹)				
86	340	377	0.48	0.51
93	432	456	0.57	0.58
106	584	597	0.70	0.71
119	715	719	0.82	0.83
133	800	818	0.92	0.93
156	914	929	1.07	1.08
175	969	978	1.17	1.17
194	984	1001	1.24	1.25
211	1011	1006	1.31	1.30
222	1014	1002	1.34	1.33
238	1009	993	1.39	1.37
261	986	970	1.43	1.42
288	935	937	1.47	1.47
317	905	897	1.51	1.51
336	886	872	1.54	1.53
351	864	852	1.56	1.55
370	838	825	1.57	1.56
$Cu(CH_3CO_2)(L)$·py (150 × 10^{-6} cm³ mol⁻¹)				
90	280	230	0.45	0.41
105	390	355	0.57	0.55
128	548	538	0.75	0.73
145	650	644	0.87	0.86
174	774	770	1.04	1.04
192	820	817	1.12	1.11
222	862	855	1.24	1.23
241	862	863	1.29	1.29
256	862	862	1.33	1.33
273	862	856	1.37	1.37
296	839	841	1.41	1.41
299	835	838	1.41	1.42
315	820	825	1.44	1.44
335	795	807	1.46	1.47
349	775	793	1.47	1.49
CuL_2·2DMSO[d] (230 × 10^{-6} cm³ mol⁻¹)				
90	17	37	0.11	0.16
108	72	85	0.25	0.27
135	200	187	0.46	0.45
164	313	315	0.64	0.64
179	371	361	0.73	0.72
197	426	420	0.82	0.81
216	476	472	0.91	0.90
243	538	528	1.02	1.01
164	564	560	1.09	1.09
290	587	582	1.17	1.16
325	599	597	1.25	1.25
342	605	599	1.29	1.28
370	605	598	1.34	1.33

[a] The temperature-independent paramagnetism ($N\alpha$) is fixed at 60 × 10^{-6} cm³ mol⁻¹. [b] The ligand diamagnetic corrections given in parentheses are taken from B. Figgis and J. Lewis, "Techniques of Inorganic Chemistry," Vol. 4, Interscience, New York, N. Y., 1965, p 142. [c] $\mu_{eff} = 2.828((\chi_M - N\alpha)T)^{1/2}$. [d] The magnetic data for CuL_2·2DMF are very similar; *viz.*, Bleaney–Bowers behavior is observed with $2J = -361$ cm⁻¹ and $g = 2.11$. [e] Calculated values based on the Bleaney–Bowers equation. Small deviations in the χ_M values for $Cu(CH_3CO_2)(L)$·py at low temperature are attributed to traces of the paramagnetic monomer.

Table II. Parameters Obtained by Fitting the Bleaney–Bowers Equation to Temperature-Dependent Magnetic Susceptibilities

	$-2J$, cm⁻¹	g
$Cu(CH_3CO_2)_2$·LH	320	2.15
$Cu(CH_3CO_2)(L)$·LH	232	2.11
$Cu(CH_3CO_2)(L)$·py	273	2.12
CuL_2·2DMSO	389	2.11

Table III. Esr Data for the Complexes[a]

	$Cu(CH_3CO_2)(L)$·LH at 9.72 GHz	$Cu(CH_3CO_2)(L)$·py at 9.72 GHz	CuL_2·2DMSO at 8.95 GHz
		296°K	
$H_{\perp_1}$	1360	1430	1920
$H_{\perp_2}$	4670	4645	4040
H_{z_2}	5560	5510	4575
$\Delta M = 2$	~600	~600	~1100
$S = ^1/_2$	~3400	~3400	~3050
D	0.27_4	0.26_8	0.18_8
$g_\perp$	2.02 ±0.02	2.02 ±0.02	2.02 ±0.02
g_z	2.30 ±0.02	2.30 ±0.02	2.28 ±0.02
		77°K	
H_{x_1}	1500	1560	2040
H_{y_1}	1230	1290	1800
H_{x_2}	4550	4540	3940
H_{y_2}	4750	4750	4110
D	0.27_4	0.26_8	0.18_8
E	0.00_7	0.00_7	0.00_7
g_x	2.01 ±0.02	2.01 ±0.02	2.01 ±0.02
g_y	2.03 ±0.02	2.03 ±0.02	2.04 ±0.02
g	2.12 ±0.02	2.12 ±0.02	2.11 ±0.02

[a] All field positions are given in gauss. The zero-field splitting parameters D and E are given in cm⁻¹.

1 level at an energy $|2J|$ above this. Satisfactory least-squares fits to the experimental results were obtained (see Table II).

Comparison of the magnetic properties of $Cu(CH_3CO_2)_2$·LH with those of the vast number of copper(II) alkanoate complexes listed in the recent tabulation of Jotham, Kettle, and Marks[18] suggests that this complex is a simple 7-azaindole adduct of copper(II) acetate with the pyridine N atoms of 7-azaindole occupying the terminal coordination sites of each dimeric unit; *cf.* pyridine in $Cu(CH_3CO_2)_2$·py, for which $2J = -325$ cm⁻¹ and $g = 2.21$.[19] However, the structures of the other complexes are not so readily assigned and further characterization is necessary.

Esr Spectra. The X-band esr spectra of powdered samples of the complexes recorded at 296 and 77°K are illustrated in Figure 1. Assignments of the observed transitions are summarized in Table III. The spectra can be interpreted using the effective spin Hamiltonian (with $S = 1$)

$$\mathcal{H} = g\beta\mathbf{H}\cdot\hat{\mathbf{S}} + D\hat{S}_z^{\,2} + E(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}) - {}^2/_3D$$

(this form of the Hamiltonian assumes that the principal axes for zero-field splitting are coincident with the **g** tensor) where D and E are the zero-field splitting parameters and x, y, and z are a principal-axes coordinate system fixed with respect to the Cu–Cu bond. When the external magnetic field is in an arbitrary direction with respect to x, y, and z, we expect to see certain $\Delta M = 1$ resonances and the *forbidden* $\Delta M = 2$ resonance, according to the conditions detailed by Wasserman, *et al.*,[20] for the spectra of randomly oriented organic triplets and adapted by Wasson, *et al.*,[21] for dimeric copper(II) compounds.

At room temperature, splitting of $H_\perp$ into H_x and H_y is either incomplete or unobservable, so an approximation to axial symmetry is made initially. With assignment of the $\Delta M = 1$ transitions H_{z_2}, $H_{\perp_1}$, and $H_{\perp_2}$, the values of g_z, $g_\perp$, and D are obtained from the relations derived in ref 20. An average g value may be calculated from the expression $g^2 = {}^1/_3(g_z^2 + 2g_\perp^2)$. The low-intensity absorption in the range 3000–3500

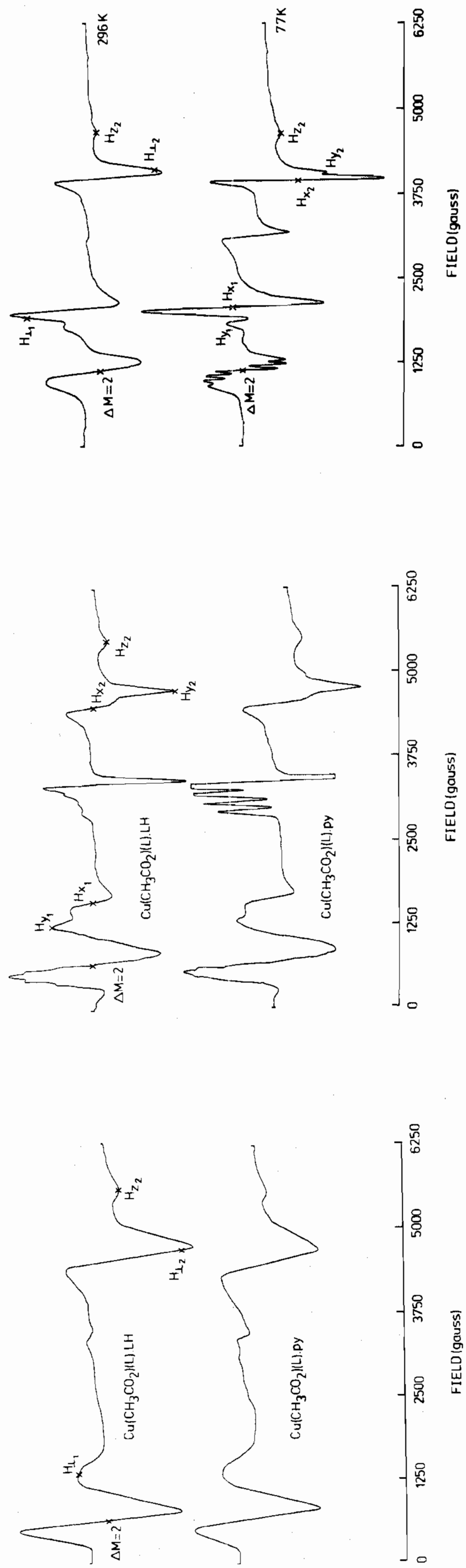

Figure 1. Esr spectra: (a) (left) $Cu(CH_3CO_2)(L)\cdot LH$ and $Cu(CH_3CO_2)(L)\cdot py$ at 296°K; (b) (center) $Cu(CH_3CO_2)(L)\cdot LH$ and $Cu(CH_3CO_2)(L)\cdot py$ at 77°K; (c) (right) $CuL_2\cdot 2DMSO$ at 296 and 77°K.

G becomes more intense as the temperature is lowered; it is almost certainly due to impurity of ground state $S = 1/2$. It can be deduced[20] that the $\Delta M = 2$ transition (which we expect to see when $D < h\nu$) and the $\Delta M = 1$ band H_{z_1} should occur close together in the low-field region. Accordingly, the band at lowest field cannot be assigned unambiguously, though its isotropic nature and its similarity to the low-field band observed in $Cu(Ad)_2\cdot 4H_2O$[14] are strongly suggestive of $\Delta M = 2$.

Important features are observed in the 77°K spectrum of each complex. As expected, all $S = 1$ band intensities become weaker. In addition, the $\Delta M = 2$ band becomes partially resolved, and in the case of $CuL_2\cdot 2DMSO$, resolution into the expected seven components is almost complete. In $Cu(CH_3CO_2)(L)\cdot LH$ and $Cu(CH_3CO_2)(L)\cdot py$, the $H_{\perp_1}$ and $H_{\perp_2}$ bands are each split into two (H_x and H_y), implying that E is nonzero (but small). It is estimated that E is about 0.01 cm^{-1}, so that $g_\perp$ is modified into x and y components. The weak band at 1800 G and the shoulder at 4110 G in the 77°K spectrum of $CuL_2\cdot 2DMSO$ are also attributed to distortion from axial symmetry. Alternative assignments do not appear to be compatible with the theory of $\Delta M = 1$ and $\Delta M = 2$ transitions.[20,21]

In line with magnetic susceptibility data, the triplet-state characteristics of the esr spectra reveal the presence of pairwise magnetic exchange in the complexes. The average g values calculated from esr powder spectra agree well with those derived from susceptibility measurements.

Infrared Spectra. The infrared spectrum of 7-azaindole has been reported in some detail and band assignments have been proposed.[16] When 7-azaindole is dissolved in low concentration in a nonpolar solvent, the N–H stretching band occurs at about 3470 cm^{-1}. In the solid, however, hydrogen bonding leads to extensive band broadening and a shift to lower energy, with a peak at about 3100 cm^{-1}. The infrared spectra of $Cu(CH_3CO_2)(L)LH$, $Cu(CH_3CO_2)(L)\cdot py$, and $CuL_2\cdot 2DMSO$ (mounted on KBr disks) are recorded in Figure 2.

In $Cu(CH_3CO_2)(L)\cdot LH$, an N–H stretching band is assigned at 3240 cm^{-1}. Though this band is considerably sharper than that observed in 7-azaindole (see Figure 3), it is still quite broad and somewhat lower in energy than the free N–H band. It is probable that hydrogen bonding occurs in the complex, *e.g.*, from N–H on the pyrrole ring to an oxygen atom of coordinated acetate. In most respects, the spectrum resembles that of ligand 7-azaindole.[16] However, infrared bands due to acetate also appear to be present. The strong band at 675 cm^{-1} is assigned to the characteristic OCO deformation.[22] In $Cu(CH_3CO_2)(L)\cdot LH$, the assignment of bands due to acetate stretching modes is complicated by the presence of 7-azaindole bands in the region of interest. There are strong bands at 1595, 1575, 1552, and 1432 cm^{-1}. The 1595- and 1432-cm^{-1} bands contain shoulders and have a broad appearance. It is difficult to assign the acetate bands precisely, but careful inspection of other metal 7-azaindole complexes prepared in this laboratory suggests that the asymmetric OCO stretching mode ω_1 is most likely to be found as part of the broad band at 1432 cm^{-1} and that the symmetric mode ω_2 most probably occurs at 1575 cm^{-1}. Bands below 1400 cm^{-1} and above 1610 cm^{-1} cannot be reasonably assigned to ω_1 and ω_2. It is likely that the mode of coordination of acetate in the complex is symmetric or unidentate with hydrogen bonding to the free oxygen atom.[23]

The infrared spectrum of the pyridine complex is similar to that of $Cu(CH_3CO_2)(L)\cdot LH$, though clearly no N–H stretch can be observed. The strong band at 670 cm^{-1} is again assigned to the OCO deformation. The stretching bands of acetate are tentatively assigned: ω_1 as part of the broad 1420-cm^{-1} band and ω_2 at 1575 cm^{-1}.

In the spectrum of $CuL_2\cdot 2DMSO$, there is no N–H stretching mode observable, confirming that 7-azaindole is

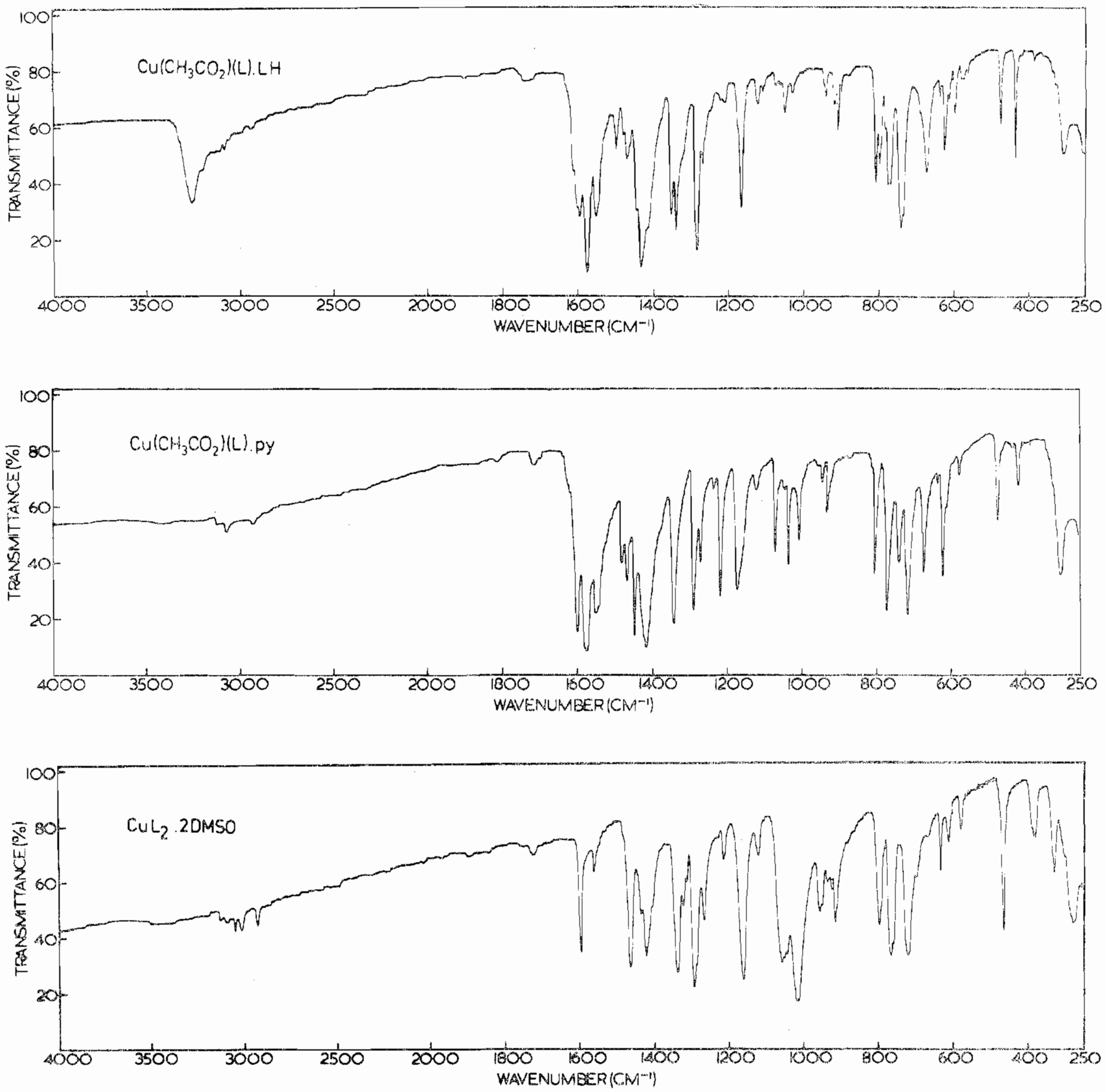

Figure 2. Infrared spectra (KBr disks): (a) (top) $Cu(CH_3CO_2)(L) \cdot LH$; (b) (center) $Cu(CH_3CO_2)(L) \cdot py$; (c) (bottom) $CuL_2 \cdot 2DMSO$.

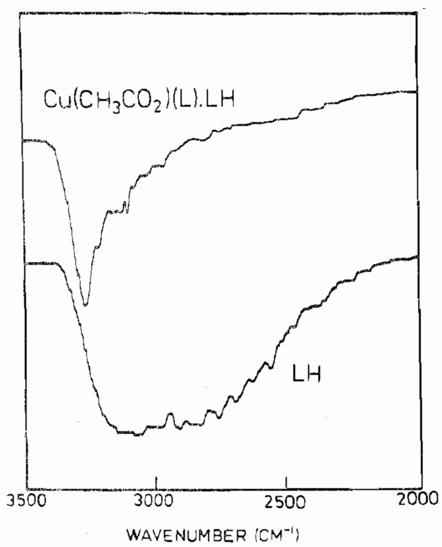

Figure 3. Infrared spectra (KBr disks) for $Cu(CH_3CO_2)(L) \cdot LH$ compared with LH in the region 2000–3500 cm^{-1}.

present in an anionic form. Assignment of the medium-intensity band at 958 cm^{-1} to CH_3 rocking in DMSO allows for assignment of the strong 1020- and 1060-cm^{-1} absorptions to S=O stretching modes.[24-26] The shift to lower frequency of these bands compared with free gaseous DMSO (1102 cm^{-1}) excludes the possibility of coordination to the metal *via* sulfur but would not be inconsistent with either hydrogen-bonded lattice DMSO or DMSO coordinated *via* oxygen. Nevertheless, the S=O band at 1060 cm^{-1} is probably associated with lattice DMSO, since the position of this absorption is higher than that usually observed in oxygen-bonded DMSO complexes (1020 cm^{-1} or less).[25] The infrared spectrum of the related compound $CuL_2 \cdot 2DMF$ is comparatively clear in the 1020–1060-cm^{-1} region. However, a strong, broad band associated with C=O stretching[27,28] is seen at 1658 cm^{-1}. The medium-intensity band at 1108 cm^{-1} is assigned to the CH_3 rocking mode.[29] Again, the position of the C=O stretching band does not allow definite decision as to whether all of the DMF molecules occupy lattice positions or whether coordination to the metal also occurs in the complex.

Electronic Spectra. Diffuse-reflectance spectra of micro crystalline samples of the complexes are summarized in Table IV. Features of the spectrum of copper(II) acetate monohydrate are also included.[30,31] There seems little doubt that the two low-energy bands in each case are associated with ligand field transitions of a $3d^9$ configuration. Gradual replacement of oxygen (acetate) donors by nitrogen (7-azaindole) donors in the coordination sphere appears to shift these d–d bands to higher energy. Because the assignment of the

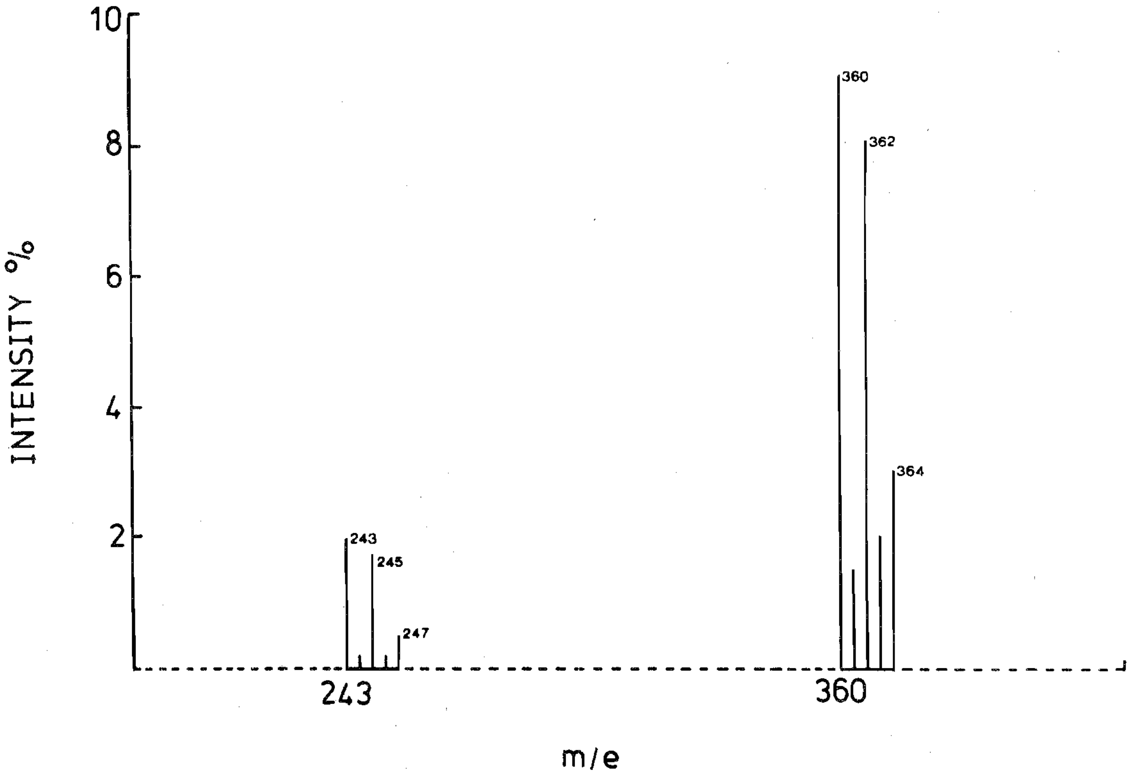

Figure 4. Cu_2 isotope patterns in the mass spectrum of $Cu(CH_3CO_2)(L)\cdot LH$.

Table IV. Diffuse-Reflectance Spectra (0–30,000 cm^{-1})

Complex	Band position, cm^{-1}	Complex	Band position, cm^{-1}
$Cu(CH_3CO_2)$-(L)·LH[a]	12,200 sh[c]	$CuL_2\cdot 2DMSO$[a]	15,200 sh
	15,500		19,200
	23,500		29,400
	29,400		
$Cu(CH_3CO_2)$-(L)·py[a]	12,500 sh	$Cu(CH_3CO_2)_2\cdot H_2O$[b]	11,000
	15,600		14,400
	24,100		27,000
	29,800		

[a] Microcrystalline samples. [b] Single-crystal data. [c] sh = shoulder.

27,000-cm^{-1} band in $Cu(CH_3CO_2)_2\cdot H_2O$ has been a matter of considerable controversy,[30,31] no attempt will be made here to assign the bands between 20,000 and 30,000 cm^{-1} in the 7-azaindole complexes.

Mass Spectra. Low-resolution mass spectra have been recorded for the complexes $Cu(CH_3CO_2)(L)\cdot LH$, $Cu(CH_3CO_2)(L)\cdot py$, and $CuL_2\cdot 2DMSO$. The major peak assignments are listed in Table V, and the Cu_2 isotope patterns for $Cu(CH_3CO_2)(L)\cdot LH$ are shown in Figure 4. In the case of $Cu(CH_3CO_2)(L)\cdot LH$, a high-resolution mass spectrum was also recorded (see Table VI), allowing for definitive assignments of the peaks at *m/e* 60, 118, and 360 to $[CH_3COOH]^+$, $[LH]^+$ (the base peak), and $[Cu_2L_2]^+$, respectively. For the pyridine complex, the base peak occurs at *m/e* 79, corresponding to $[py]^+$, whereas for $CuL_2\cdot 2DMSO$, the ion $[Cu_2L_2]^+$ becomes the base peak. In each case, the fragmentation pattern suggests a molecular structure containing at least two anionic 7-azaindole bridges per Cu atom pair.

The peak of highest mass number observed in $Cu(CH_3CO_2)(L)\cdot LH$ and $Cu(CH_3CO_2)(L)\cdot py$ is due to $[Cu_2L_2]^+$, and peaks corresponding to a dimeric molecular ion or the ion $[Cu_2(CH_3CO_2)_2(L)_2]^+$ cannot be located. We have also recorded the mass spectrum of binuclear $Cu(CH_3CO_2)_2\cdot py$. Interestingly, its major features are very similar to those above. In particular, the peak of highest mass number observed corresponds to the ion $[Cu_2(CH_3CO_2)_2]^+$.

Table V. Mass Spectral Peak Assignments

m/e	Ion	Rel intens, %
	$Cu(CH_3CO_2)(L)\cdot LH$ (150°)[a]	
360	$[Cu_2L_2]^+$	9
243	$[Cu_2L]^+$	2
180	$[CuL]^+$	5
118	$[LH]^+$	100
91	$[LH - HCN]^+$	38
70	Metastable, $118^+ \rightarrow 91^+$	
60	$[CH_3COOH]^+$	23
45	$[OCOH]^+$	23
43	$[CH_3CO]^+$	26
	$Cu(CH_3CO_2)(L)\cdot py$ (150°)	
360	$[Cu_2L_2]^+$	20
243	$[Cu_2L]^+$	3
180	$[CuL]^+$	4
118	$[LH]^+$	38
91	$[LH - HCN]^+$	8
79	$[py]^+$	100
70	Metastable, $118^+ \rightarrow 91^+$	
60	$[CH_3COOH]^+$	30
52	$[py - HCN]^+$	90
45	$[OCOH]^+$	38
43	$[CH_3CO]^+$	54
34	Metastable, $79^+ \rightarrow 52^+$	
	$CuL_2\cdot 2DMSO$ (230°)	
476	$[Cu_2L_2(L - H)]^+$	
360	$[Cu_2L_2]^+$	100
243	$[Cu_2L]^+$	17
180	$[CuL]^+$	71
118	$[LH]^+$	88
91	$[LH - HCN]^+$	42
70[b]	Metastable, $118^+ \rightarrow 91^+$	

[a] The temperature of the probe is given in parentheses. [b] Below *m/e* 70, other peaks are evident, *e.g.*, *m/e* 63 and 39. These are probably associated with further fragmentation of 7-azaindole.

In $CuL_2\cdot 2DMSO$, the dominant peak corresponds to the recurring ion $[Cu_2L_2]^+$. Peaks of higher mass number become apparent when the highest possible gain is used. The peaks correspond to the progression $[Cu_4L_4]^+ \rightarrow [Cu_4L_3]^+ \rightarrow [Cu_3L_3]^+ \rightarrow [Cu_3L_2]^+ \rightarrow [Cu_2L_2]^+$, suggesting dimerization

Table VI. High-Resolution Mass Spectral Data for $Cu(CH_3CO_2)(L){\cdot}LH$

m/e	Measd mass	Calcd mass	Assigned formula	Rel intens, %
360	359.950313	359.950141	$C_{14}H_{10}N_4{}^{63}Cu_2$	9
118	118.053133	118.053096	$C_7H_6N_2$	100
60	60.020991	60.021127	$C_2H_4O_2$	23

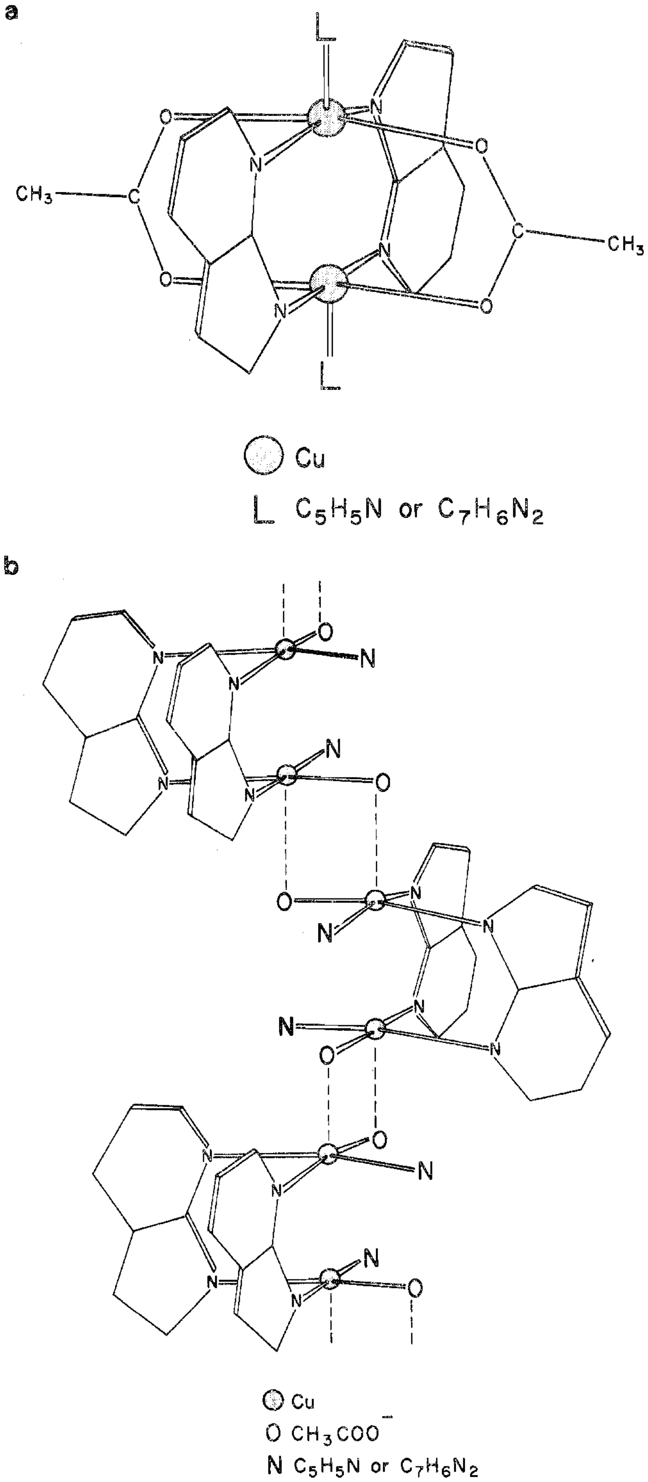

Figure 5. Alternative molecular structures for $Cu(CH_3CO_2)(L){\cdot}LH$ and $Cu(CH_3CO_2)(L){\cdot}py$: (a) binuclear; (b) chain.

of $[Cu_2L_2]^+$ ions in the mass spectrometer to form $[Cu_4L_4]^+$. In addition, a peak at *m/e* 476 with a typical Cu_2 isotope pattern is evident at high gain. Whereas the other high-mass ions are quickly lost, the *m/e* 476 ion appears to be comparatively stable. This peak corresponds to $[Cu_2L_2(L - H)]^+$ and is entirely analogous to the $[Ni_2L_2(L - H)]^+$ ion which we observed[15] in the mass spectrum of the dimer Ni_2L_4. Although a dimeric ion of the type $[Cu_2L_4]^+$ could not be located, the appearance of the *m/e* 476 peak in the spectrum of $CuL_2{\cdot}2DMSO$ suggests that this complex may exhibit a binuclear structure.

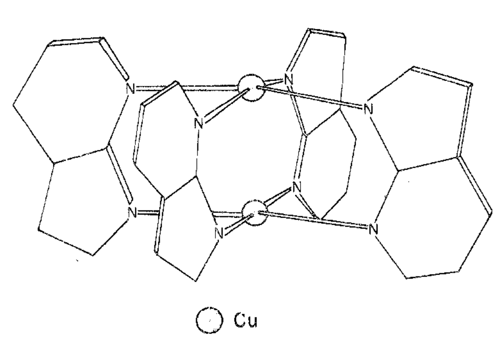

Figure 6. Proposed molecular structure for $CuL_2{\cdot}2DMSO$.

Conclusions

Magnetic susceptibility data for the four complexes clearly indicate that essentially pairwise antiferromagnetic exchange occurs in each case. The sign and strength of exchange observed in $Cu(CH_3CO_2)_2{\cdot}LH$ is typical of the binuclear copper(II) alkylcarboxylate series, suggesting that the complex is a simple 7-azaindole adduct of dimeric copper(II) acetate.

The structures of $Cu(CH_3CO_2)(L){\cdot}LH$ and $Cu(CH_3CO_2)(L){\cdot}py$ cannot be assigned with such certainty. As demonstrated by Yawney, *et al.*,[32] the observation of pairwise antiferromagnetic exchange does not prove a binuclear structure. These workers carried out an X-ray structural determination of the complex copper(II) propionate–*p*-toluidine. They found that it exhibited a one-dimensional chain structure containing two crystallographically independent copper atoms (Cu(1) and Cu(2)). Each of these is bound in a square-pyramidal configuration to four carboxylate oxygen atoms and to the nitrogen atom of a *p*-toluidine molecule. Two of the four independent carboxylate groups function as bidentate ligands, bridging Cu(1) and Cu(2) in a syn,syn configuration. The remaining two propionate groups are monodentate and form monatomic oxygen bridges from a basal site of one copper atom to the apical site of its centrosymmetric equivalent. The Bleaney–Bowers magnetic behavior of the complex was rationalized in terms of a pairwise interaction between Cu(1) and Cu(2) for which the principal pathway is an indirect one involving the triatomic carboxylate bridges.

We believe that the complexes $Cu(CH_3CO_2)(L){\cdot}LH$ and $Cu(CH_3CO_2)(L){\cdot}py$ may be assigned either the familiar copper(II) acetate monohydrate dimeric structure[3] or the copper(II) propionate–*p*-toluidine chain structure (see Figure 5). Molecular model studies indicate that neither structure can be eliminated on steric grounds. The binuclear structure involves the bridging of isolated pairs of copper atoms by two acetate anions and two 7-azaindole anions in syn,syn configurations. If the complexes adopt the chain structure of Yawney, *et al.*, then we propose that only the acetate ions will function as monatomic bridges, necessitating that the anions of 7-azaindole act as triatomic bridges. Bridging of the deprotonated pyrrole nitrogen of 7-azaindole to two metal atoms would appear to be unfavorable because of the concomitant loss of planarity (and resonance energy) of the 7-azaindole anion.

For this reason, we consider it unlikely that the inner complex $CuL_2{\cdot}2DMSO$ adopts the copper(II) propionate–*p*-toluidine chain structure. Rather, $CuL_2{\cdot}2DMSO$ appears to be dimeric; *cf.* Ni_2L_4 (see Figure 6) and a structural analog of the dimers $Cu_2(CH_3CO_2)_4(H_2O)_2$, $Cu_2(dpt)_4$, and

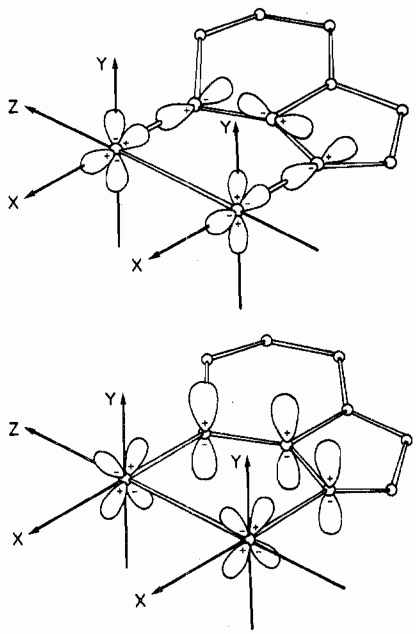

Figure 7. Relationship between bridging NCN and copper(II) orbitals in CuL_2·2DMSO: (a) (top) σ system; (b) (bottom) π system.

$[Cu_2(Ad)_4(H_2O)_2]\cdot 6H_2O$. We are unable to distinguish whether both of the DMSO molecules (per copper) are contained within the lattice or whether one of these is involved in axial coordination to copper.

The mechanism by which spin coupling occurs in binuclear structures of the kind proposed for CuL_2·2DMSO is still a matter of considerable interest and speculation.[33] The two types of exchange mechanism usually proposed, *viz.*, direct exchange and superexchange, have been well reviewed.[33-36] In the present context (CuL_2·2DMSO), these mechanisms may be detailed as follows (the symbol ∥ denotes overlap): (i) direct exchange as a consequence of overlap between singly occupied $d_{x^2-y^2}$ orbitals of the two metal atoms (δ overlap), *viz.*, $d_{x^2-y^2}(Cu_1)\|d_{x^2-y^2}(Cu_2)$; (ii) superexchange resulting from the overlap of singly occupied metal $d_{x^2-y^2}$ orbitals with the σ system of the anionic 7-azaindole ligand, *viz.*, $d_{x^2-y^2}(Cu_1)\|$-$\sigma(NCN)\|d_{x^2-y^2}(Cu_2)$, where σ(NCN) signifies an anionic 7-azaindole molecular orbital of σ symmetry. It is possible to construct several molecular orbitals of this type. According to the *x*, *y*, and *z* coordinate axes defined in Figure 7, the nitrogen and carbon atomic orbitals on the triatomic NCN group relevant to σ molecular orbital construction are 2s, $2p_x$, and $2p_z$. An example of σ overlap through the NCN bridging group is depicted in Figure 7a.

In the above discussion, the singly occupied metal orbital is assumed to be $3d_{x^2-y^2}$, but this is really an oversimplification of the case. In fact, the relevant metal orbital may contain admixtures of other 3d orbitals if the symmetry about copper is low or if spin–orbit coupling is invoked. If such admixtures are sufficiently large, the mixing of the following pathways should be considered: (i) direct exchange *via* $d_{z^2}(Cu_1)\|d_{z^2}(Cu_2)$ σ overlap; (ii) superexchange involving the π system of the anionic 7-azaindole ligand, *e.g.*, $d_{xy}(Cu_1)\|\pi(NCN)\|d_{xy}(Cu_2)$. In this situation, the $2p_y$ orbitals of the nitrogen and carbon will be involved (see Figure 7b).

As is always the case in such systems, the contribution of each possible mechanism to the overall exchange cannot be easily estimated, even when precise structural data are available. A major reason for this is the lack of detailed knowledge regarding the metal and ligand wave functions in the binuclear complex.

As a final note, it is instructive to compare the strength of magnetic exchange $|2J|$ observed in the 7-azaindole complexes reported here with that observed in other complexes involving triatomic bridges. This comparison is made in Table VII. Even allowing for differences in the Cu–Cu distance (and hence direct exchange) from compound to compound, it is apparent that the efficiency of superexchange varies amongst the triatomic bridging systems. The structural similarities between the NCN groups in the anions of adenine and 7-azaindole suggest that the Cu–Cu separation in CuL_2·2DMSO will be similar to that observed in $Cu(Ad)_2\cdot 4H_2O$ (2.95 Å). Though direct exchange may be present in copper(II) acetate monohydrate (where the Cu–Cu separation is 2.64 Å), its contribution at 2.95 Å should be considerably smaller. Thus, we conclude that the anionic 7-azaindole bridging system is an efficient transmitter of spin interaction, *viz.*, in CuL_2·2DMSO, $2J = -389\ cm^{-1}$; *cf.* copper(II) acetate monohydrate for which $2J = -286\ cm^{-1}$.

Table VII. Comparison of Magnetic Exchange Parameters in Copper(II) Complexes Which Exhibit Pairwise Exchange

Complex	$2J$, cm^{-1}	Structure type	Cu-Cu, Å	Ref
$Cu(dpt)_2$	diamag	Dimeric	2.44	2, 5
$Cu(CH_3CO_2)_2\cdot H_2O$	−286	Dimeric	2.64	3, 13
$Cu(CH_3CO_2)_2\cdot py$	−325	Dimeric	2.64	19, 37
$Cu(C_2H_5CO_2)_2\cdot p$-tol	−105	Chain	3.20 3.27 3.34	32
$Cu(Ad)_2\cdot 4H_2O$	−257	Dimeric	2.95	8, 14
$Cu(CH_3CO_2)_2\cdot LH$	−320	Dimeric		Present work
$Cu(CH_3CO_2)(L)\cdot LH$	−232	Dimeric or chain		Present work
$Cu(CH_3CO_2)(L)\cdot py$	−273	Dimeric or chain		Present work
$CuL_2\cdot 2DMSO$	−389	Dimeric		Present work

Registry No. $Cu(CH_3CO_2)_2\cdot LH$, 53260-34-7; $Cu(CH_3CO_2)(L)\cdot LH$, 53320-09-5; $Cu(CH_3CO_2)(L)\cdot py$, 53320-10-8; $CuL_2\cdot 2DMSO$, 53320-12-0; $CuL_2\cdot 2DMF$, 53320-13-1.

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Contribution from Philips Research Laboratories, Eindhoven, The Netherlands

Interaction of Bivalent Metal Ions with Their Chelates of Ethylenedinitrilotetraacetic Acid (EDTA) and 1,2-*trans*-Cyclohexylenedinitrilotetraacetic acid (CDTA)

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An interaction of bivalent metal ions with their EDTA and CDTA complexes was established by means of spectrophotometry for Cu^{2+} and by means of nmr for Zn^{2+}. The competition between protons and metal ions in their reaction with metal chelates was demonstrated for Cu^{2+} and Zn^{2+} by aid of infrared spectroscopy and for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} by pH measurements. Evidence is presented for the formation of binuclear copper chelates of CDTA and it is proposed that the formation of binuclear chelates of bivalent metal ions with EDTA and CDTA is a general phenomenon. Whereas a symmetrical structure, with the metal ions in equivalent positions, may be achieved for binuclear EDTA complexes, this is obviously impossible for the CDTA complexes. From the known values of stability constants the formation of symmetrical binuclear EDTA complexes is, however, improbable except for Cu^{2+}. The intensity of the visible absorption band of the mononuclear EDTA complex of copper was found to be strongly temperature dependent. This is thought to reflect an equilibrium between complexes, differing in the number of water molecules, bound to the Cu^{2+} ion. Attention is drawn to the parallelism in spectral changes of CuEDTA observed on cooling and on protonation; both changes are imputed to a change in the number of coordinated water molecules. For the corresponding CDTA complex no temperature dependence of the light absorption was found, indicating the absence of a notable change in the coordination of the Cu^{2+} ion.

Introduction

On account of the preference for six-coordination of bivalent metal ions the bonding of more than one metal ion to one ligand molecule is not unexpected for ligands with more than six donor atoms. For example, binuclear complexes of diethylenetriaminepentaacetic acid (DTPA) or triethylenetetraminehexaacetic acid (TTHA) and ligands of the type $(CH_2COOH)_2N(CH_2)_nN(CH_2COOH)_2$ with $n \geq 3$ have been reported.[1-3] The formation of 2:1 bivalent metal–EDTA and –CDTA complexes is less obvious.

The existence of binuclear EDTA complexes in liquid solution has often been neglected or even denied.[4,5] However, the proposed formation of binuclear complexes of Ca^{2+} and Sr^{2+}, deduced from nmr experiments,[6] is an exception. A symmetrical configuration has been proposed for these complexes. In crystalline complexes symmetrical as well as asymmetrical configurations have been observed. In the symmetrical configuration as found for $Cu_2Y{\cdot}4H_2O$[7] (H_4Y represents EDTA) both metal ions are bound to an iminodiacetate fragment of the EDTA molecule; in the asymmetrical configuration as observed in $Sn_2Y{\cdot}4H_2O$[8] one metal ion is fully coordinated by the EDTA molecule whereas the second ion is bound to carboxylate oxygen atoms and water molecules.

The existence of heteronuclear 2:1 complexes of CDTA (H_4Cy) has been proposed by Margerum in explaining the rate-suppressing influence of Pb^{2+} or Cu^{2+} ions on proton-catalyzed exchange reactions.[9] For CDTA symmetrical binuclear complexes are very unlikely, owing to the rigidity of the ligand molecule.

Observations will be reported from which the interaction of a number of bivalent metal ions with their EDTA and CDTA complexes could be deduced. The formation of Cu_2Cy was established and of Cu_2Y made probable. Absorption spectra of binuclear, protonated, and normal copper chelates will be given and the structure of these chelates will be discussed.

Experimental Section

All chemicals were reagent grade. Solutions of metal perchlorates were prepared by treating the basic carbonates $MCO_3{\cdot}M(OH)_2$ with perchloric acid (M represents a bivalent metal). The pH of the solutions was adjusted with NaOH or $HClO_4$. The ionic strength was controlled with $NaClO_4$. Deuterium oxide, which was used as a solvent in the infrared measurements, contained 99.75% D_2O. Solutions in D_2O were obtained by evaporation of the corresponding aqueous solutions and dissolution of the residue in D_2O. The evaporation followed by dissolution in D_2O was repeated twice. The pD of the solutions was obtained from a pH meter reading by employing the empirical equation[10]

$$pD = pH_{\text{meter reading}} + 0.40$$

Infrared spectra were recorded on a Hitachi EPI-G grating