3.58 Å. For square-planar coordination the crystal stereochemical arrangement with the metal halogen bonds directed perpendicular to the plane of the 2,5-dmp is that which would be expected and which results in minimum steric interaction between the methyl groups and the halogen atoms.

The nickel–ligand distances are shorter than might be expected. The Ni–Br distance 2.31 Å. is 0.2 Å. less than the sum of the bromine single bond radius and the octahedral covalent radius of nickel(II) applicable to the square-planar configuration (1.39 + 1.14 = 2.53 Å.).[2] The Ni–N distance at 1.85 Å. is also 0.2 Å. less than the sum of the appropriate radii (1.39 + 0.7 = 2.09 Å.). The Ni–N distance is, however, consistent with that found in dimethylglyoxime[8] (1.89 Å.) and in nickel phthalocyanine[9] (1.83 Å.). All other intramolecular interatomic distances and angles are shown in Fig. 2.

Acknowledgments.—We are grateful to Dr. B. Lever for presenting us with the problem and with crystals. We are also grateful to Mrs. Jean Dollimore, O. S. Mills, J. S. Rollett, and R. A. Sparks for making available computer programs. P. J. P. and G. B. R. are grateful to the U. S. Department of the Army through its European Research Office for support of this work.

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Magnetic Studies with Copper(II) Salts. VI. Variable Singlet–Triplet Energies in Amine-Substituted Copper(II) Alkanoates[1,2]

By E. Kokot and R. L. Martin[3]

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The magnetic susceptibility at temperatures between 80 and 350°K. is reported for a new series of monoamine adducts of copper(II) acetate and butyrate. Antiferromagnetic rather than Curie-type behavior is observed, from which the separation between singlet and triplet states of the dimeric species is deduced. Pyridine-type bases resemble water or dioxane in giving mono derivatives of copper(II) alkanoates with singlet–triplet separations of about 300 cm.$^{-1}$. In marked contrast, aniline-type bases reduce this interval to only 100 cm.$^{-1}$. The electronic spectra of these adducts in the region 8000–3250 Å. contain only the weak absorption bands at 7000 Å. (band I) and 3750 Å. (band II) generally observed for binuclear copper(II) alkanoates. The observed sensitivity of band I and insensitivity of band II to changes of the axially situated amine does not, at this stage, lead to the desired elucidation of the electronic spectrum.

Introduction

The copper(II) acetate monohydrate dimer, $Cu_2(CH_3CO_2)_4(H_2O)_2$, provides a singularly favorable example for testing current concepts of homopolar bonding by d electrons. The singlet ground state of the binuclear molecule is believed to arise predominantly from direct overlap of 3d–3d orbitals between pairs of contiguous copper atoms so that the ensuing d–d bond will have σ, π, or δ symmetry about the Cu–Cu internuclear axis. The bond is rather weak and measurements of the variation with temperature of magnetic susceptibility[4] and of paramagnetic resonance[5,6] establish that a triplet state for the molecule lies only some 300 cm.$^{-1}$ above the singlet ground state.

Figgis and Martin[4] recognized that the unusual geometric features of copper acetate coupled with the 3d^9 electron configuration of divalent copper conferred upon it favorable conditions for the formation of a unique class of metal-to-metal bond, namely a δ-bond. Support for this postulate was derived from estimates of the relevant overlap integrals. In particular, it was concluded that calculated overlaps were so small that the relative order of d orbital energies in the homonuclear diatomic species Cu_2^{4+} (for which the σ-bonding configuration about the Cu–Cu axis is certainly lowest; see Fig. 1) would almost certainly be inverted by the ligand field of ten neighboring oxygen atoms. This field was somewhat arbitrarily assumed to approximate to that of $[Cu(H_2O)_6]^{2+}$, the promotional energy of a positive hole $3d_{z^2} \leftarrow 3d_{x^2-y^2}$ being taken as 12,000 cm.$^{-1}$ after Polder.[7] A valence bond rather than molecular orbital description of the Cu–Cu binding was deliberately preferred as being more appropriate to the small magnitude of the overlap integrals involved.

The concept of δ-bonding in copper(II) acetate was strongly supported by Ross,[8] who demonstrated that

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(1) Part V of this series: R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

(2) This work is taken from a thesis presented by E. Kokot to the School of Chemistry, University of New South Wales, in partial fulfillment of the requirements for the Ph.D. degree, March, 1961.

(3) Department of Inorganic Chemistry, University of Melbourne, Melbourne, Australia.

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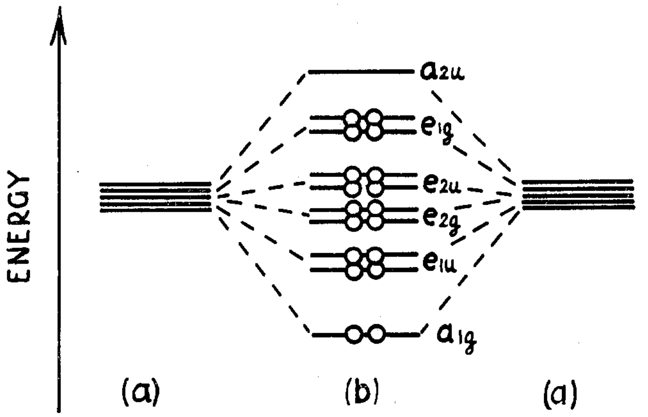

Fig. 1.—Schematic energy levels for diatomic species Cu_2^{4+} not drawn to scale: (a) 3d energy levels for gaseous Cu^{2+} ion; (b) molecular orbital energy levels. Point group symmetry $D_{\infty h}$.

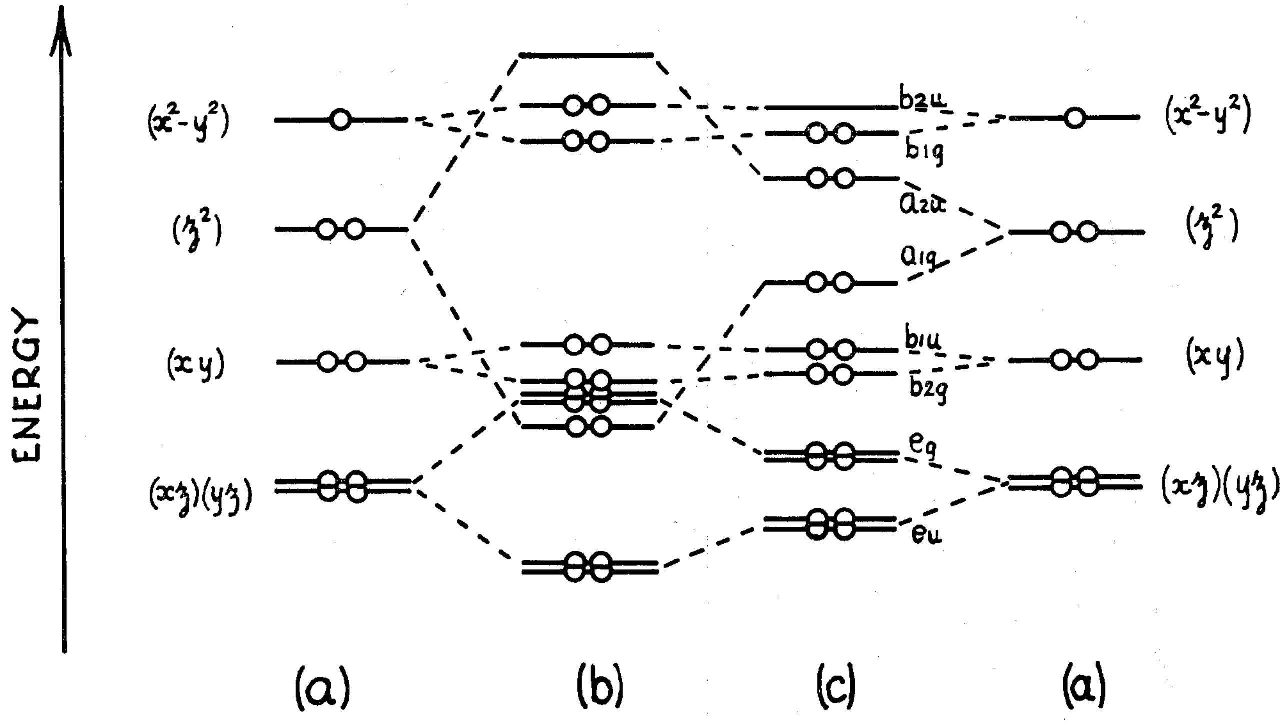

Fig. 2.—Highest molecular orbitals for $[Cu_2(CH_3CO_2)_4(H_2O)_2]$ not drawn to scale. Point group symmetry D_{4h}. (a) 3d energy levels for $CuSO_4 \cdot 5H_2O$ after Holmes and McClure[10]; (b) Cu–Cu σ-bonding[9]; (c) Cu–Cu δ-bonding.[4]

the experimental values of the magnetic splitting parameters g_z and $g_x = g_y$ were eminently consistent with the δ-bonded model. For σ-bonding g_z has to be 2; for δ-bonding it can exceed 2. From the paramagnetic resonance spectra experimental values of $g_z = 2.42$ and 2.34 are obtained.[5,6]

More recently Forster and Ballhausen[9] have reconsidered the electronic structure of the dimer using a molecular orbital (LCAO) scheme. Again the hazardous assumption is made that the ligand field resembles that of $CuSO_4 \cdot 5H_2O$ both in symmetry and strength. However, these authors follow the later work of Holmes and McClure[10] rather than of Polder by employing a very much reduced value of 1000 cm.$^{-1}$ for the promotional energy $3d_{z^2} \leftarrow 3d_{x^2-y^2}$ to obtain the molecular orbital scheme (Fig. 2b) on which is based their contrary proposal that a rather strong σ-bond exists between the two copper atoms. Further, they considered that all of the experimental features of copper(II) acetate, namely, antiferromagnetism, electronic absorption spectrum, and g-factors, could be thereby qualitatively explained.

Unfortunately, the u and g symmetry labels for the π-type molecular orbitals have been incorrectly assigned by Forster and Ballhausen in their scheme. Tonnet, Yamada, and Ross[11] have explored the consequences of this error, the correction of which leads to the expectation of additional electronic transitions of energy below 28,000 cm.$^{-1}$; these are not seen in the spectrum.[12] These authors further consider that the calculation of g-factors by Forster and Ballhausen (on which they mainly base their claim that σ-bonding is involved) is in error by a factor of 2 for the orbital component. Tonnet, Yamada, and Ross reaffirm their support for the δ-bonded model (Fig. 2c) but note that the electronic absorption spectrum of crystalline copper acetate, even at 77°K., continues to resist a convincing interpretation.

In this paper our previous studies[13-15] are extended to new nitrogenous derivatives of copper(II) acetate designed to evaluate further those factors which determine the nature of the Cu–Cu bonding. In particular, the preparation of a series of binuclear amine derivatives,

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TABLE I

MAGNETIC DATA, $\chi_M(T)$ AND $\mu(T)$, FOR $[Cu(RCO_2)_2amine]_2$

$[Cu(CH_3CO_2)_2(pyridine)]_2$

Temp., °K.	96.7	110.1	124.7	147.7	178.8	200.5	225.7	249.3	284.1	309.2	335.1
$10^6\chi_g$	0.381	0.643	0.854	1.41	1.95	2.29	2.54	2.67	2.75	2.75	2.68
$10^6\chi_M$	219	287	342	487	628	717	782	816	836	836	819
μ, B.M.	0.352	0.449	0.532	0.713	0.904	1.03	1.15	1.23	1.33	1.39	1.43

$[Cu(CH_3CO_2)_2(\alpha\text{-picoline})]_2$

Temp., °K.	97.2	125.5	156.6	190.5	226.4	265.7	298.3	321.1	334.5	346.0
$10^6\chi_g$	0.366	0.920	1.58	2.02	2.32	2.46	2.50	2.51	2.50	2.47
$10^6\chi_M$	236	397	588	717	804	843	855	859	854	847
μ, B.M.	0.371	0.584	0.816	1.00	1.17	1.30	1.38	1.44	1.46	1.48

$[Cu(CH_3CO_2)_2(\beta\text{-picoline})]_2$

Temp., °K.	99.2	132.0	171.8	211.7	248.2	279.2	306.3	332.0
$10^6\chi_g$	0.395	1.11	1.92	2.36	2.58	2.62	2.62	2.60
$10^6\chi_M$	240	437	659	780	840	852	851	846
μ, B.M.	0.379	0.633	0.910	1.11	1.25	1.34	1.40	1.45

$[Cu(CH_3CO_2)_2(\gamma\text{-picoline})]_2$

Temp., °K.	97.5	142.0	179.8	219.0	254.7	285.3	312.0	340.6
$10^6\chi_g$	0.359	1.37	1.99	2.39	2.63	2.68	2.67	2.66
$10^6\chi_M$	226	503	675	784	849	865	863	861
μ, B.M.	0.362	0.712	0.944	1.13	1.27	1.36	1.42	1.48

$[Cu(C_3H_7CO_2)_2(pyridine)]_2$

Temp., °K.	99	150.2	202.9	235.7	268.5	300.6	326.5	347.5
$10^6\chi_g$	0.186	0.949	1.67	1.91	2.06	2.09	2.09	2.06
$10^6\chi_M$	227	469	698	774	820	831	829	820
μ,B.M.	0.365	0.704	1.02	1.16	1.28	1.37	1.42	1.46

$[Cu(C_3H_7CO_2)_2(\alpha\text{-picoline})]_2$

Temp., °K.	96.8	151.0	202.7	235.0	269.3	299.9	327.0	346.5
$10^6\chi_g$	0.059	0.802	1.47	1.70	1.87	1.89	1.90	1.93
$10^6\chi_M$	158	443	664	740	796	803	808	815
μ B.M.	0.277	0.683	0.993	1.18	1.31	1.39	1.46	1.42

$[Cu(C_3H_7CO_2)_2(\beta\text{-picoline})]_2$

Temp., °K.	100	145.2	183.2	221.0	252.0	267.5	286.0	308.2	333.2	350.6
$10^6\chi_g$	0.054	0.784	1.33	1.69	1.85	1.90	1.90	1.95	1.94	1.90
$10^6\chi_M$	161	439	621	740	791	809	809	826	820	809
μ, B.M.	0.286	0.666	0.910	1.10	1.22	1.27	1.31	1.38	1.43	1.46

$[Cu(C_3H_7CO_2)_2(\gamma\text{-picoline})]_2$

Temp., °K.	94.5	127.2	170.0	196.8	233.2	264.5	294.5	330.5	348.0
$10^6\chi_g$	0.120	0.577	1.25	1.61	1.86	1.90	1.97	1.94	1.90
$10^6\chi_M$	218	369	592	712	793	807	829	822	808
μ, B.M.	0.346	0.563	0.853	1.02	1.17	1.26	1.35	1.42	1.45

$[Cu(C_3H_7CO_2)_2(aniline)]_2$

Temp., °K.	85.0	99.6	121.0	151.0	177.2	222.3	269.0	305.5	333.6
$10^6\chi_g$	6.39	6.13	5.90	5.34	5.00	4.28	3.65	3.30	3.01
$10^6\chi_M$	2298	2215	2137	1951	1830	1601	1393	1277	1180
μ, B.M.	1.24	1.31	1.42	1.52	1.59	1.66	1.70	1.73	1.74

$[Cu(C_3H_7CO_2)_2(p\text{-toluidine})]_2$

Temp., °K.	94.7	122.5	154.3	181.0	214.9	253.2	295.1	332.5
$10^6\chi_g$	6.64	6.32	5.58	4.95	4.41	3.83	3.39	3.01
$10^6\chi_M$	2477	2369	2112	1896	1708	1511	1357	1228
μ, B.M.	1.36	1.51	1.60	1.64	1.69	1.72	1.76	1.77

$[Cu(C_3H_7CO_2)_2(m\text{-toluidine})]_2$

Temp., °K.	92.5	111.5	146.4	177.7	211.0	251.5	293.5	337.7
$10^6\chi_g$	6.78	6.43	5.71	5.07	4.53	3.91	3.46	3.04
$10^6\chi_M$	2523	2403	2157	1936	1749	1536	1379	1235
μ, B.M.	1.35	1.45	1.57	1.64	1.69	1.73	1.77	1.79

$[Cu_2(RCO_2)_4(amine)_2]$ with R = CH_3 or $n\text{-}C_3H_7$, has been achieved with both pyridine- and aniline-type bases. The near vertical singlet–triplet excitation energy arising from spin–spin coupling between pairs of copper atoms has been obtained from the variation of magnetic susceptibility with temperature. The electronic spectra of the compounds have been recorded.

Experimental

Materials. (a) **$[Cu_2(CH_3CO_2)_4(amine)_2]$ where the Amine is Pyridine, α-Picoline, β-Picoline, or γ-Picoline.**—Treatment of powdered anhydrous copper(II) acetate with a solution of freshly distilled amine in dioxane yielded a dark blue solution from which blue or violet solids (diamines and tetramines) crystallized over a period of 48 hr. When the crystals were left for several days at reduced pressure over concentrated sulfuric acid, they lost all but one molecule of amine to form emerald-green copper acetate monoamine derivatives. Copper acetate–pyridine.[16] *Anal.* Calcd. for $C_9H_{11}O_4NCu$: C, 41.47; H, 4.25; N, 5.37; Cu, 24.39. Found: C, 41.55; H, 4.00; N, 5.32; Cu, 24.25. Copper acetate–α-picoline. *Anal.* Calcd. for $C_{10}H_{13}O_4NCu$: C, 43.69; H, 4.77; N, 5.10; Cu, 23.14. Found: C, 43.53; H, 4.53; N, 4.99; Cu, 23.27. Copper acetate–β-picoline. *Anal.* Found: C, 43.40; H, 4.71; N, 5.02; Cu, 23.20. Copper acetate–γ-picoline. *Anal.* Found: C, 43.45; H, 4.76; N, 5.23; Cu, 23.07.

(b) **$[Cu_2(C_3H_7CO_2)_4(\text{amine})_2]$ where the Amine is Pyridine, α-Picoline, β-Picoline, or γ-Picoline.**—Copper butyrate was dissolved in benzene which contained amine in slight excess of the equimolar quantity. The solutions were filtered and concentrated by evaporation until crystallization occurred. The crystals were rapidly transferred to a desiccator, in which the adhering benzene and amine were removed at reduced pressure over calcium chloride. Copper butyrate–pyridine. *Anal.* Calcd. for $C_{13}H_{19}O_4NCu$: C, 49.26; H, 6.04; N, 4.42; Cu, 20.06. Found: C, 49.48; H, 5.82; N, 4.53; Cu, 20.11. Copper butyrate–α-picoline. *Anal.* Calcd. for $C_{14}H_{21}O_4NCu$: C, 50.81; H, 6.38; N, 4.23; Cu, 19.22. Found: C, 50.72; H, 6.44; N, 4.39; Cu, 19.36. Copper butyrate–β-picoline. *Anal.* Found: C, 50.86; H, 6.37; N, 4.31; Cu, 19.31. Copper butyrate–γ-picoline. *Anal.* Found: C, 50.81; H, 6.22; N, 4.37; Cu, 19.8.

(c) **$[Cu_2(C_3H_7CO_2)_4(\text{amine})_2]$ where the Amine is Aniline, *p*-Toluidine, or *m*-Toluidine.**—Anhydrous copper butyrate was treated with a slight excess of amine in benzene. Slow evaporation at room temperature yielded crystals which were washed with benzene and dried under reduced pressure. Copper butyrate–aniline. *Anal.* Calcd. for $C_{14}H_{21}O_4NCu$: C, 50.81; H, 6.38; N, 4.23; Cu, 19.22. Found: C, 50.83; H, 6.48; N, 4.39; Cu, 19.18. Copper butyrate–*p*-toluidine. *Anal.* Calcd. for $C_{15}H_{23}O_4NCu$: C, 52.22; H, 6.72; N, 4.06; Cu, 18.44. Found: C, 52.18; H, 6.64; N, 4.16; Cu, 18.48. Copper butyrate–*m*-toluidine. *Anal.* Found: C, 52.44; H, 6.46; N, 4.01; Cu, 18.35.

Copper was estimated iodometrically using 0.01 *N* sodium thiosulfate solution while carbon, hydrogen, and nitrogen were determined by standard microanalytical procedures.

Magnetic Measurements.—The techniques and corrections applied in this work are essentially those described in previous parts of this series. The magnetic moment, μ, was calculated from the expression $\mu = 2.839[(\chi_M - N\alpha)T]^{1/2}$ where an allowance of $N\alpha = 60 \times 10^{-6}$ was made for the temperature-independent contribution to the paramagnetism per gram-ion of copper. The experimental data tabulated in Tables I and III represent mean values of independent measurements made at two field strengths, approximately 5000 and 8000 gauss. The diamagnetic correction Δ was determined experimentally on samples of the free acids and ligands. Data for copper sulfate, copper acetate, and copper butyrate are included for comparison.

Absorption Spectra in Visible and Near-Ultraviolet Regions.—The absorption spectra of the amine derivatives of copper(II) butyrate dissolved in benzene (concentration, 0.005 *M*) were recorded between 3250 and 8000 Å, a Cary Model 11 MS-50 recording spectrophotometer being used (cell path length, 2 cm). The wave length maxima of the two absorption bands, I and II, which characterize the binuclear species are listed in Table II; data for the molar extinction coefficients, ϵ_I and ϵ_{II}, based on monomeric formula weights, and values for the ratio ϵ_I/ϵ_{II} are also included. Typical spectra are illustrated in Fig. 3.

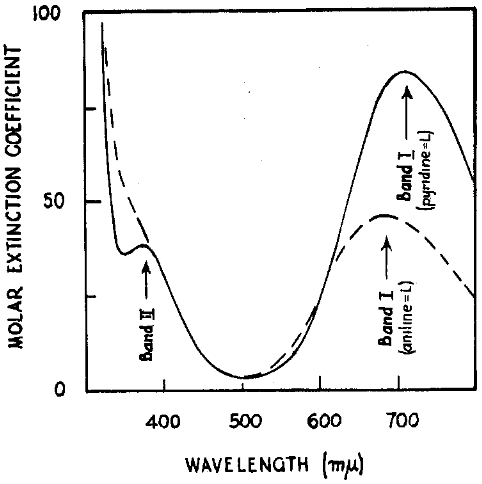

Fig. 3.—Absorption spectra in benzene of dimeric copper(II) butyrate with aniline or pyridine in the axial positions.

TABLE II

ELECTRONIC ABSORPTION BANDS FOR $[Cu(C_3H_7CO_2)_2L]_2$ IN BENZENE SOLUTION

$[Cu(C_3H_7CO_2)_2L]_2$ L	Band I λ_{max}, Å.	ϵ_I[a]	Band II λ_{max}, Å.	ϵ_{II}[a]	ϵ_I/ϵ_{II}
0	6750	100	3700	50	2.0
Pyridine	7120	84	3750	38	2.2
α-Picoline	7120	74	3750	36	2.1
β-Picoline	7180	85	3750	38	2.2
γ-Picoline	7180	84	3780	38	2.2
Aniline	6780	49	3750	38	1.3
m-Toluidine	6810	49	3810	48	1.0
p-Toluidine	6780	49	3750	45	1.1
Dioxane	6600	230	3750	65	3.5
Ethanol	6600	130	3750	90	1.4

[a] Extinction coefficients are calculated from molarities based on monomeric formula weights.

Discussion

Magnetic Properties.—The magnetic moments at room temperature of the new amine derivatives of copper(II) acetate and copper(II) butyrate are listed in Table III.

Two types of behavior can be discerned. The eight derivatives of the pyridine-type bases have depressed moments which lie in the narrow range $\mu = 1.34 \pm 0.02$ B.M. which may be compared with the subnormal magnetic moments of $\mu = 1.38 \pm 0.03$ B.M. which characterize the binuclear anhydrous and hydrated copper(II) *n*-alkanoates.[13] There is no significant change in passing from acetate to butyrate, and coordination of pyridine or its methyl-substituted derivatives in terminal positions L (see Fig. 4) does not modify the room temperature moment.

On the other hand, the introduction of aniline-type bases at the terminal positions affects the magnetic moment in a striking manner. The values for five aniline-type bases are raised to $\mu = 1.75 \pm 0.02$ B.M. which, although corresponding to the "spin-only" value for divalent copper, are, in fact, well below the value of 1.9 B.M. normally observed for Cu^{2+} ion in magnetically dilute systems. The magnitude of these differences is more clearly revealed by comparing the magnetic molar susceptibility χ_M at room temperature, the appropriate ranges being: copper acetate–pyridine series, $\chi_M = 843 \pm 23 \times 10^{-6}$ c.g.s.e.m.u.; copper butyrate–pyridine series, $\chi_M = 821 \pm 13 \times 10^{-6}$ c.g.s.e.m.u.;

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(16) O. Foerster, *Ber.*, **25**, 3420 (1892).

TABLE III

MAGNETIC PROPERTIES OF COPPER(II) ALKANOATES AT ROOM TEMPERATURE

Compound[a]	Color	Temp., °C.	$10^6\chi_g$	$-10^6\Delta$	$10^6\chi_M$	μ, B.M.
$CuSO_4 \cdot 5H_2O$	Blue	20.0	5.90	122	1595	1.91
$Cu(CH_3CO_2)_2$	Blue-green	22.2	4.39	72	869	1.39
$Cu(CH_3CO_2)_2 \cdot H_2O$	Blue-green	21.0	4.03	85	889	1.40
$Cu(C_3H_7CO_2)_2$	Blue-green	17.2	3.14	120	866	1.37
$Cu(C_3H_7CO_2)_2 \cdot H_2O$	Blue-green	23.7	2.67	133	816	1.35
$Cu(CH_3CO_2)_2 \cdot$py	Green	17.0	2.76	119	839	1.35
$Cu(CH_3CO_2)_2 \cdot$ α-pic	Green	19.0	2.50	130	817	1.34
$Cu(CH_3CO_2)_2 \cdot$ β-pic	Green	17.5	2.63	131	853	1.36
$Cu(CH_3CO_2)_2 \cdot$ γ-pic	Green	17.0	2.68	128	854	1.36
$Cu(C_3H_7CO_2)_2 \cdot$py	Green	17.5	2.09	168	830	1.34
$Cu(C_3H_7CO_2)_2 \cdot$ α-pic	Green	17.5	1.89	178	803	1.32
$Cu(C_3H_7CO_2)_2 \cdot$ β-pic	Green	17.5	1.95	179	824	1.34
$Cu(C_3H_7CO_2)_2 \cdot$ γ-pic	Green	18.5	1.97	178	829	1.34
$Cu(CH_3CO_2)_2 \cdot$an	Green	23.0	4.00	134	1314	1.73
$Cu(CH_3CO_2)_2 \cdot$ *p*-tol	Green	22.5	4.33	140	1392	1.78
$Cu(CH_3CO_2)_2 \cdot 2$*p*-tol	Dark green	25.6	3.17	208	1466	1.84
$Cu(C_3H_7CO_2)_2 \cdot$an	Green	17.0	3.45	185	1326	1.73
$Cu(C_3H_7CO_2)_2 \cdot$ *m*-tol	Green	17.5	3.49	186	1326	1.73
$Cu(C_3H_7CO_2)_2 \cdot$ *p*-tol	Green	20.0	3.36	188	1365	1.76

[a] py, pyridine; pic, picoline; an, aniline; tol, toluidine.

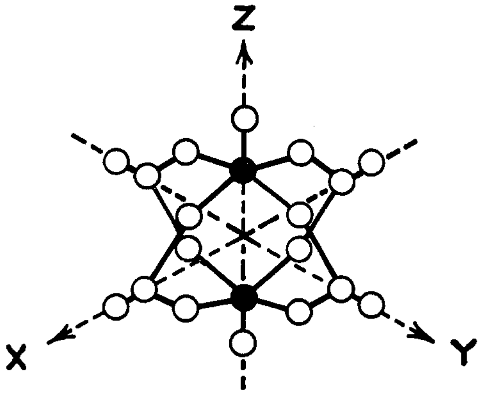

Fig. 4.—Molecular structure of $[Cu_2(RCO_2)_4L_2]$ with reference axes marked.

copper butyrate–aniline series, $\chi_M = 1363 \pm 31 \times 10^{-6}$ c.g.s.e.m.u.; magnetically dilute $[Cu(H_2O)_6]^{2+}$, $\chi_M = 1500 \times 10^{-6}$ c.g.s.e.m.u.

The anomalous temperature variation of the magnetic susceptibility exhibited by the pyridine series (Fig. 5) closely parallels the curves for the parent acetate and butyrates and so confirms the retention of the bimolecular configuration $[Cu_2(RCO_2)_4(\text{amine})_2]$ illustrated in Fig. 4. Barclay and Kennard,[17] using crystals of the compound $[Cu_2(CH_3CO_2)_4(\text{pyridine})_2]$ prepared by us, have established by X-ray methods that the intramolecular Cu–Cu distance (2.63 Å.) is nearly identical with that (2.64 Å.) in $[Cu_2(CH_3CO_2)_4(H_2O)_2]$.[18] However, an independent X-ray structure[19] analysis of the pyridinate unexpectedly indicates that the dimeric unit can be crystallized in a dimorphic form (see Table IV) with an apparently significantly greater Cu–Cu distance of 2.70 Å. The magnetic data reported here refer to the monoclinic form.

TABLE IV

X-RAY CRYSTAL DATA FOR DIMORPHIC FORMS OF $[Cu(CH_3CO_2)_2(\text{pyridine})]_2$

	Ref. 17	Ref. 19
Symmetry	Monoclinic	Orthorhombic
a, Å.	12.52	13.08
b, Å.	17.31	8.59
c, Å.	9.96	19.57
β	96° 43′	
Space group	A2/a (C^6_{2h}, No. 15)	Pbca
Cu–Cu distance, Å.	2.63	2.70
No. of molecules/unit cell	4	4

The corrected molar magnetic susceptibility of the aniline-type series also varies with temperature in the same characteristic anomalous manner (see Fig. 5), but for this series the maximum in susceptibility is incipient rather than fully developed. However, the experimental data can also be fitted closely by the formula

$$\chi_m = \frac{g^2 N\beta^2}{3kT}\left[1 + {}^1/_3 \exp(J/kT)\right]^{-1} + N\alpha \quad (1)$$

previously used[4] to describe the anomalous temperature variation of magnetic susceptibility for compounds with the molecular configuration of copper acetate. The curve of best fit for the aniline series requires a maximum in susceptibility at about 90°K., *i.e.*, at the lower limit of our cryostat equipment.

Since the temperature of maximum susceptibility, T_c, cannot be measured directly for the aniline derivatives, an arbitrary figure for *g* has been selected by iterative procedures which minimizes differences be-

TABLE V

ESTIMATED VALUES OF *g*, T_c, AND *J* for $[Cu(C_3H_7CO_2)_2L]_2$

$[Cu(C_3H_7CO_2)_2L]_2$ L	*g*	100°K. T_c, °K.	100°K. *J*, cm.$^{-1}$	300°K. T_c, °K.	300°K. *J*, cm.$^{-1}$
Aniline	2.18	103	114	112	124
m-Toluidine	2.18	91	101	90	100
p-Toluidine	2.18	91	101	90	100

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[17] G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 5244 (1961).

[18] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

[19] F. Hanic, D. Stempelova, and K. Hanicova, *Chem. Zvesti*, **15**, 102 (1961).

tween the values of T_c calculated at two extreme temperatures, 100 and 300°K. This procedure gives excellent agreement between calculated T_c and J values at the two selected temperatures (see Table V).

The calculated equations for magnetic susceptibility (shown as full lines in Fig. 5) then become as shown below. Copper(II) acetate pyridine series

$$\chi_M = [0.635/T][1 + {}^1/_3\exp(481/T)]^{-1} + 60 \quad (2)$$

Copper(II) butyrate pyridine series

$$\chi_M = [0.606/T][1 + {}^1/_3\exp(480/T)]^{-1} + 60 \quad (3)$$

Copper(II) butyrate aniline series

$$\chi_M = [0.592/T][1 + {}^1/_3\exp(152/T)]^{-1} + 60 \quad (4)$$

Clearly, the terminal substituent exerts a marked effect on the singlet–triplet energy interval; the significant quantities are set out in Table VI. The mean values fall in the ranges shown below. Copper acetate pyridine series

$T_c = 298 \pm 9$°K.; $g = 2.27 \pm 0.05$; $J = 329 \pm 8$ cm.$^{-1}$

Copper butyrate pyridine series

$T_c = 300 \pm 5$°K.; $g = 2.21 \pm 0.03$; $J = 333 \pm 9$ cm.$^{-1}$

Copper butyrate aniline series

$T_c = 97 \pm 6$°K.; $g = 2.18 \pm 0.00$; $J = 112 \pm 12$ cm.$^{-1}$

These mean values include appreciable random scatter due to such factors as irreproducibility of packing of the polycrystalline samples in Gouy tubes, the difficulty of selecting a value of T_c from broad maxima in χ_M–T curves, the fact that T_c is not directly observed for the aniline series, and variations of the singlet–triplet separation with temperature. Even so, the evidence that the singlet–triplet interval is reduced by about 200 cm.$^{-1}$ (*i.e.*, 70%) with aniline-type bases is unambiguous.

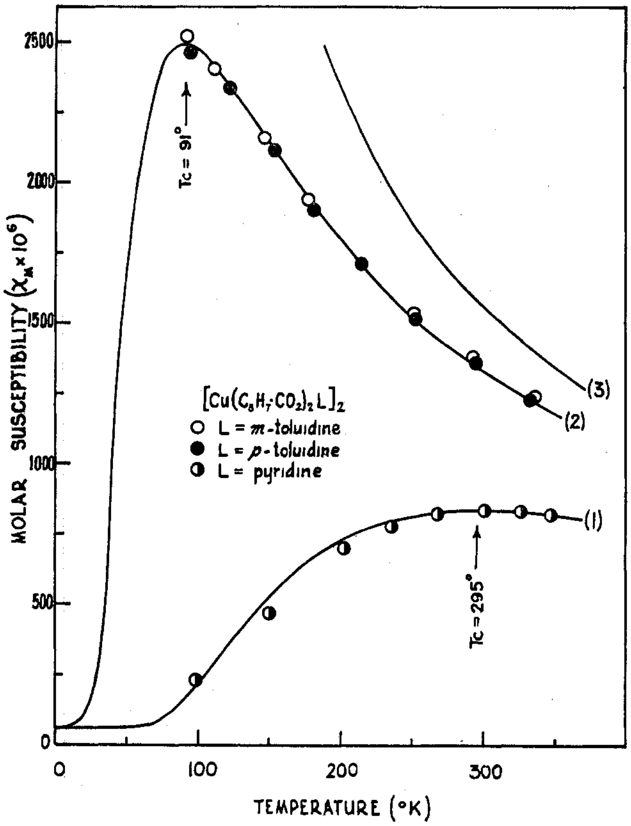

Fig. 5.—Variation of molar susceptibility (χ_M) with temperature. Curve 1 calculated from eq. 3; curve 2 calculated from eq. 4; curve 3 calculated for $CuSO_4 \cdot 5H_2O$ (μ = 1.90 B.M.). Experimental data as shown.

Table VI

Singlet–Triplet Energies for $[Cu(RCO_2)_2L]_2$

R	L	T_c, °K.	g	J cm.$^{-1}$	J kcal. mole^{-1}
CH_3	0	270	2.17	300	0.86
CH_3	H_2O	255	2.13	284	0.82
C_3H_7	0	290	2.23	322	0.92
C_3H_7	H_2O	305	2.22	339	0.97
CH_3	Pyridine	295	2.22	325	0.98
CH_3	α-Picoline	310	2.30	342	0.99
CH_3	β-Picoline	292	2.31	322	0.92
CH_3	γ-Picoline	295	2.25	325	0.93
C_3H_7	Pyridine	295	2.21	325	0.93
C_3H_7	α-Picoline	300	2.18	331	0.95
C_3H_7	β-Picoline	305	2.24	337	0.96
C_3H_7	γ-Picoline	300	2.22	331	0.95
C_3H_7	Aniline	107	2.18	119	0.35
C_3H_7	*p*-Toluidine	91	2.18	101	0.29
C_3H_7	*m*-Toluidine	91	2.18	101	0.29

Electronic Spectra.—The electronic spectra of copper(II) alkanoates are characterized by two well-defined and well-separated regions of absorption at about 7000 Å. (band I) and 3750 Å. (band II).[12] The molar extinction coefficients of these bands for anhydrous copper(II) butyrate in benzene solution are about 100 and 50, respectively.[14] Tonnet, Yamada, and Ross[11] note that a third very intense (presumably charge-transfer) band is located at 2500 Å. (band III).

The conclusion that the present amine derivatives retain the binuclear structure of the monohydrate is further strengthened by the fact that their absorption spectra between 3250 and 8000 Å. in benzene solution contain both the bands I and II (Fig. 3). Band I in the red region is of unusually high intensity for divalent copper compounds (*e.g.*, copper butyrate in water, λ_{max} 7750 Å., ϵ 22; copper butyrate in dioxane, λ_{max} 6600 Å., ϵ 230)[14] which supports the suggestion of Ross[8] that any close resemblance between the spectra of binuclear copper alkanoates and mononuclear Cu^{2+} species such as $[Cu(H_2O)_6]^{2+}$ is coincidental.

Band I appears at λ_{max} 7150 ± 30 Å. for the pyridine series (ϵ_I 80 ± 6) and is not only displaced to shorter wave lengths by substitution of the aniline-type bases, λ_{max} 6750 ± 15 Å., but is also weakened in intensity (ϵ_I 49). On the other hand, band II occurs with roughly the same intensity not only for both pyridine- and aniline-type derivatives (ϵ_{II} 37 ± 1 and ϵ_{II} 43 ± 5, respectively) but also for a variety of other terminal substituents such as dioxane (ϵ ~65) and benzene (ϵ_{II} ~50).

This invariance of position and intensity of band II for copper butyrate with terminal ligands of varying donor strengths (*e.g.*, for benzene, dioxane, ethanol, pyridine, and aniline, λ_{max} is 3750 Å. and ϵ_{II} falls in the range 65 ± 25) led us to suspect that this band might arise from weak absorption within a bridging alkanoate entity. However, this possibility can be safely excluded for we find that the spectrum in chloroform of basic beryllium acetate, $Be_4O(CH_3CO_2)_6$, in which pairs of beryllium atoms are bridged by the oxyanion, is transparent down to 2440 Å.

In contrast, band I is sensitive to the nature of the solvent (Table II). It is therefore tempting to infer[20] that band I might contain the positive hole promotions $(xz, yz) \leftarrow (x^2\text{–}y^2)$ and/or $(z^2) \leftarrow (x^2\text{–}y^2)$ with the invariant band II involving the $(xy) \leftarrow (x^2\text{–}y^2)$ transition. While such an assignment is consistent with the polarization measurements of Yamada, *et al.*[12] (band I x, y polarized; band II z polarized), if there is vibronic coupling, it is at variance with the clear identification[11] of band I with the hole promotion $(xy) \leftarrow (x^2\text{–}y^2)$ deduced from the experimental g-factors. Accordingly, it must be conceded at this stage that the assignment of the electronic spectrum remains unresolved.

Influence of Terminal Ligands on Singlet–Triplet Separation.—The origin of the remarkable effect of aniline-type bases in reducing the singlet–triplet separation from 300 to 100 cm.$^{-1}$ is a matter for speculation. It seems reasonable to assume that the Cu–Cu distance will be determined primarily by the dimensions of the butyrate group and so remain reasonably constant and unaffected by the nature of the terminal substituent L. Accordingly, the singlet–triplet energy interval appears to be singularly sensitive to differences in the Cu–N bond type in the pyridine and aniline series.

The successful induction of the binuclear configuration of copper(II) formate which can be achieved by pyridine- but not aniline-type bases again emphasizes the importance of subtle differences between these two types of nitrogenous ligand.[1,15] It is generally agreed that pyridine coordinates to transition metal ions both more frequently and more strongly than aromatic amines, for whereas aniline can only form a classical dative link to the metal, pyridine can potentially form a multiple bond through participation of quinonoid-type structures. Certainly double bonding, even though not necessarily extensive, immediately provides in principle a mechanism by which an excessive accumulation of negative charge on the metal from the $N^{\delta+}$–$Cu^{\delta-}$ σ-bond can be, in part, alleviated by means of the $N^{\delta-}$–$Cu^{\delta+}$ π-bond of the reverse polarity. In the case of aniline no such mechanism can exist.

On the other hand, the electron charge density on nitrogen may be of even more importance than its potential double-bonding capacity. For example, it is well known that pyridine, a heteroaromatic substance, resembles nitrobenzene in that the heteroatom attracts electrons from the π-layer, *i.e.*, is "π-deficient," the deficiency referring to the C atoms of the ring. In contrast, aniline has been termed "π-excessive" in that the heteroatom releases electrons from its lone pair to the π-layer of the ring, thereby lowering its capacity to form a strong coordinate link to copper. This is further substantiated by theoretical calculations[21] which suggest that the net charge on the nitrogen atom in aniline is extremely small (+0.09e) whereas that on the nitrogen atom in pyridine is much higher (−0.59e).

On this basis the effects of terminal substituents with a high net charge such as pyridine, dioxane, and water on the magnetic behavior of the binuclear molecule should be of comparable magnitude whereas those of the aniline-type bases should be of a different and lower order. The remarkable uniformity of the magnetic properties within either series of amine derivatives suggests that any influence on the singlet–triplet separation, arising from the substitution of H by CH_3 groups, is either absent or so small as not to be observable.

It was not possible to prepare other monoamines of copper(II) acetate of high purity in the present work. Typical green derivatives with α,α'-lutidine, aniline, p-toluidine, and piperidine were isolated in a slightly impure state, and their magnetic behavior (based on analytical copper values) conformed with that of the analogous compounds reported above.

The bis(p-toluidine) derivative of copper(II) acetate has a room temperature moment of 1.84 B.M. and obeys a Curie–Weiss law with $\theta \sim 20°$ (see Fig. 5). An unobtainable report of a similar green crystalline complex salt, $[Cu(CH_3CO_2)_2(p\text{-}ClC_6H_4NH_2)_2]\cdot H_2O$, has has appeared in the literature.[22]

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