COPPER(II) COMPLEXES WITH SUBNORMAL MAGNETIC MOMENTS

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CONTENTS

I. INTRODUCTION

The copper(II) ion ($3d^9$) has one unpaired electron in the 3d shell, and its compounds were considered to have magnetic moments close to the spin-only value, 1.73 B.M., irrespective of the bond type involved. Actually, the observed values of the magnetic moment are 1.9–2.2 B.M. for most copper(II) compounds with ionic or rather weak covalent bonds and 1.72–1.82 B.M. for the compounds with strong covalent bonds, the $3d4s4p^2$ type (132a, 163, 166). Thus, copper(II) compounds having subnormal magnetic moments, less than 1.73 B.M., are a distinct novelty. Recently, a large number of copper(II) compounds have been reported which have subnormal moments at room temperature and are considered in most cases to possess rather weak covalent bonds.

It is the purpose of this review to discuss these recent data. The compounds with subnormal magnetic moments most studied are dimeric, containing two copper(II) ions in a molecule. Copper(II) acetate monohydrate is a typical example of this type. Although this compound has been studied extensively no definite conclusion has been drawn about the nature of the copper–copper bond, the cause of the subnormal magnetic moment, and the assignment of the new absorption band at 375 mμ.

The compounds with subnormal magnetic moments can be classified roughly into the following two groups based on their structure. The first group, illustrated by copper(II) acetate, consists of four three-atom bridges, usually carboxylate groups, uniting two contiguous copper(II) ions. The data for them are presented in Table I.

The second group employs monatomic bridges joining copper(II) ions. These monatomic bridges may be monatomic anions, as in CuO, or an atom of a ligand, as in acetylacetone-mono(*o*-hydroxyanil)copper(II). Table II contains the magnetic data for those compounds known or believed to have monatomic bridges. Table II also contains the data for a few compounds the structures of which have not been determined.

These compounds with subnormal magnetic moments can also be classified based on the type of mechanisms of magnetic interaction. Two types of interaction
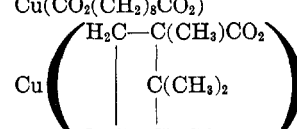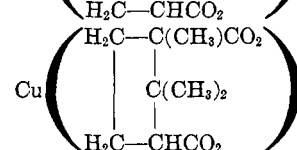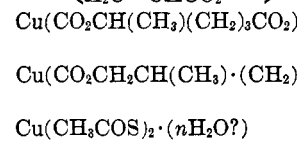
TABLE I

MAGNETIC PROPERTIES OF COPPER(II) COMPOUNDS CONTAINING TRIATOMIC BRIDGING UNITS

Ligand	Formula of compounds[a]	T, °K.	$x_g \times 10^6$,[b] c.g.s., e.m.u.	$x_a \times 10^6$, c.g.s., e.m.u.	μ,[b] B.M.	J cm.[-1]	J kcal. mole[-1]	References
Acetic acid	$Cu(CH_3CO_2)_2$[t,v]	295	4.39	869	1.39	302		45 (3, 158)
						300	0.86	10
	$Cu(CH_3CO_2)_2 \cdot H_2O$[t,v]	290	3.99	875	1.43			99 (3, 21, 45, 48, 52, 64, 114, 127, 140, 155
						284	0.82	10 (45, 141, 183)
Acetic acid, dioxane	$Cu(CH_3CO_2)_2 \cdot 0.5(C_4H_8O_2)$	292	3.41	866	1.38			136
	$Cu(CH_3CO_2)_2 \cdot C_4H_8O_2$[t,v]	293	2.40	770	1.30			136
Acetic acid, triphenyl-phosphine oxide	$Cu(CH_3CO_2)_2 \cdot (C_6H_5)_3PO$	299	(1.55)	959	1.52			57
Acetic acid, urea	$Cu(CH_3CO_2)_2 \cdot H_2NCONH_2$	290	2.96	810	1.37			99, 102
	$Cu(CH_3CO_2)_2 \cdot H_2NCONH_2 \cdot H_2O$	290	2.79	835	1.39			99, 102
Propionic acid	$Cu(C_2H_5CO_2)_2$[t,v]	289	3.61	854	1.36	300	0.86	134 (3, 158)
	$Cu(C_2H_5CO_2)_2 \cdot H_2O$[t,v]	291	3.47	899	1.40	300	0.86	134 (3)
Propionic acid, urea	$Cu(C_2H_5CO_2)_2 \cdot H_2NCONH_2$	291	2.61	825	1.39			79
Butyric acid	$Cu(C_3H_7CO_2)_2$[t,v]	290	3.14	866	1.37	322	0.92	134 (3)
	$Cu(C_3H_7CO_2)_2 \cdot H_2O$[t,v]	297	2.67	816	1.35	339	0.97	134
						300		183
Butyric acid, pyridine	$Cu(C_3H_7CO_2)_2 \cdot C_5H_5N$[t,v]	293	...	...	1.37	300		136
Butyric acid, aniline	$Cu(C_3H_7CO_2)_2 \cdot C_6H_5NH_2$[t,v]	...	...	...	1.8	100		136
Butyric acid, urea	$Cu(C_3H_7CO_2)_2 \cdot H_2NCONH_2$	291	2.43	870	1.42			79
Valeric acid	$Cu(C_4H_9CO_2)_2$	293	2.84	899	1.41			134 (3)
Valeric acid, urea	$Cu(C_4H_9CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	2.44	875	1.43			79
Caproic acid	$Cu(C_5H_{11}CO_2)_2$	293	2.23	835	(1.40)			3
Caproic acid, urea	$Cu(C_5H_{11}CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	2.05	840	1.40			79
	$Cu(C_5H_{11}CO_2)_2 \cdot H_2NCONH_2$	291	1.81	830	1.39			79
Enanthic acid	$Cu(C_6H_{13}CO_2)_2$	293	2.00	850	(1.42)			3
Enanthic acid, urea	$Cu(C_6H_{13}CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	1.89	860	1.42			79
Caprylic acid	$Cu(C_7H_{15}CO_2)_2$	293	1.71	830	(1.40)			3
Caprylic acid, urea	$Cu(C_7H_{15}CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	1.69	860	1.42			79
Pelargonic acid	$Cu(C_8H_{17}CO_2)_2$	293	1.58	850	(1.42)			3
Pelargonic acid, urea	$Cu(C_8H_{17}CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	1.42	825	1.39			79
Capric acid	$Cu(C_9H_{19}CO_2)_2$	293	1.39	845	(1.41)			3
Capric acid, urea	$Cu(C_9H_{19}CO_2)_2 \cdot 0.5(H_2NCONH_2)$	291	1.39	875	1.43			79
Undecanoic acid	$Cu(C_{10}H_{21}CO_2)_2$	293	1.37	895	(1.45)			3
Lauric acid	$Cu(C_{11}H_{23}CO_2)_2$[t,v]	293	1.32	890	1.40	278	0.79	134 (3, 55)
Lauric acid, pyridine	$Cu(C_{11}H_{23}CO_2)_2 \cdot C_5H_5N$	291	...	928	(1.48)			55
Myristic acid	$Cu(C_{13}H_{27}CO_2)_2$	293	0.95	865	(1.43)			3
Palmitic acid	$Cu(C_{15}H_{31}CO_2)_2$	293	0.83	895	(1.45)			3
Stearic acid	$Cu(C_{17}H_{35}CO_2)_2$[t,v]	290	0.842	846	1.36	278	0.79	134 (3)
						338		183
Behenic acid	$Cu(C_{21}H_{43}CO_2)_2$[t,v]	291	0.708	900	1.40	302	0.86	134
Monochloro-acetic acid	$Cu(ClCH_2CO_2)_2$	289	(3.27)	923	1.42			114 (158)
	$Cu(ClCH_2CO_2)_2 \cdot 4H_2O$	287	(2.53)	973	1.45			114

TABLE I (*Continued*)

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$,[b] c.g.s., e.m.u.	$\chi_a \times 10^6$, c.g.s., e.m.u.	μ,[b] B.M.	J cm.$^{-1}$	kcal. mole^{-1}	References
Dichloroacetic acid	$Cu(Cl_2CHCO_2)_2$	289	(3.66)	1310	1.66			114
	$Cu(Cl_2CHCO_2)_2 \cdot 4H_2O$	288	(2.99)	1360	1.74			114
Trichloroacetic acid	$Cu(Cl_3CCO_2)_2$	288	(3.22)	1420	1.77			114
	$Cu(Cl_3CCO_2)_2 \cdot 3H_2O$	289	(3.12)	1590	1.89			114
Monobromo-acetic acid	$Cu(BrCH_2CO_2)_2$	Room temp.	...	*ca.* 960	1.5			158
Trifluoroacetic acid	$Cu(F_3CCO_2)_2$	296	...	...	1.9			89
Phenylacetic acid	$Cu(C_6H_5CH_2CO_2)_2$	297	(2.24)	923	1.44			114 (158)
Diphenylacetic acid	$Cu((C_6H_5)_2CHCO_2)_2$	288	(1.25)	885	1.38			114
α-Naphthyl-acetic acid	$Cu(C_{10}H_7CH_2CO_2)_2$	288	(1.63)	958	1.44			144
Benzoic acid	$Cu(C_6H_5CO_2)_2$, α-form, pale greenish blue	291	3.6₅	1260	1.7₂			80, 81
	β-form, bluish green	291	2.66	955	1.49			80, 81 (158)
	γ-form, bluish green	291	2.28	840	1.40			80, 81
	$Cu(C_6H_5CO_2)_2 \cdot 3H_2O$	291	3.67	1500	1.87			80, 81
	$Cu(C_6H_5CO_2)_2 \cdot C_6H_5CO_2H$	291	1.48	845	1.40			80, 81
Benzoic acid, ethanol	$Cu(C_6H_5CO_2)_2 \cdot C_2H_5OH$	291	1.89	840	1.40			80, 81
Benzoic acid, urea	$Cu(C_6H_5CO_2)_2 \cdot H_2NCONH_2$	291	1.85	850	1.41			80, 81
m-Bromo-benzoic acid	$Cu(BrC_6H_4CO_2)_2$	Room temp.	...	1250	(1.74)			158
	$Cu(BrC_6H_4CO_2)_2 \cdot 3H_2O$	Room temp.	...	1536	(1.93)			158
p-Bromo-benzoic acid	$Cu(BrC_6H_4CO_2)_2$	Room temp.	...	1027	(1.58)			158
	$Cu(BrC_6H_4CO_2)_2 \cdot 5H_2O$	Room temp.	...	1031	(1.58)			158
o-Chloro-benzoic acid	$Cu(ClC_6H_4CO_2)_2 \cdot 2H_2O$	Room temp.	...	1051	(1.60)			158
o-Toluic acid	$Cu(CH_3C_6H_4CO_2)_2$	Room temp.	...	1080	(1.62)			158
m-Toluic acid	$Cu(CH_3C_6H_4CO_2)_2$	Room temp.	...	960	(1.53)			158
p-Toluic acid	$Cu(CH_3C_6H_4CO_2)_2$	Room temp.	...	942	(1.51)			158
o-Hydroxy-benzoic acid (salicylic acid)	$Cu(HOC_6H_4CO_2)_2$, green[c]	298	2.12	865	1.44			78
	$Cu(HOC_6H_4CO_2)_2$, blue-green[c]	298	2.01	830	1.41			78
	$Cu(HOC_6H_4CO_2)_2$, brown[c]	298	3.89	1460	1.87			78
	$Cu(HOC_6H_4CO_2)_2 \cdot 4H_2O$, blue green plate[d]	297	1.65	880	1.45			78 (158)
	$Cu(HOC_6H_4CO_2)_2 \cdot 4H_2O$, pale blue needle[d]	295	3.32	1560	1.92			78
m-Hydroxy-benzoic acid	$Cu(HOC_6H_4CO_2)_2 \cdot H_2O$	Room temp.	...	1030	(1.58)			158
p-Hydroxy-benzoic acid	$Cu(HOC_6H_4CO_2)_2 \cdot 5H_2O$	Room temp.	...	1711	(2.03)			158
Acetylsalicylic acid	$Cu(CH_3COOC_6H_4CO_2)_2 \cdot 1.5H_2O$	Room temp.	...	*ca.* 850	(1.43)			158
o-Nitrobenzoic acid	$Cu(O_2NC_6H_4CO_2)_2 \cdot 6H_2O$	Room temp.	...	1118	(1.65)			158
m-Nitro-benzoic acid	$Cu(O_2NC_6H_4CO_2)_2 \cdot H_2O$	Room temp.	...	1744	(2.05)			158
p-Nitrobenzoic acid	$Cu(O_2NC_6H_4CO_2)_2 \cdot 2H_2O$	Room temp.	...	1012	(1.56)			158
α-Naphthoic acid	$Cu(C_{10}H_7CO_2)_2$	Room temp.	...	1126	(1.65)			158
β-Naphthoic acid	$Cu(C_{10}H_7CO_2)_2$	Room temp.	...	948	(1.51)			158
Cinnamic acid	$Cu(C_6H_5CH:CHCO_2)_2$	Room temp.	...	938	(1.51)			158
Oxalic acid	$Cu(CO_2CO_2)$	288	(3.90)	625	1.20			6, 7
	$Cu(CO_2CO_2) \cdot 0.5H_2O$	295	(3.88)	664	1.25			7 (158)

TABLE I (Continued)

Ligand	Formulas of compounds[a]	T, °K.	$x_g \times 10^6$,[b] c.g.s., e.m.u.	$x_a \times 10^6$, c.g.s., e.m.u.	μ,[b] B.M.	J cm.$^{-1}$	J kcal. mole^{-1}	References
Malonic acid	$Cu(CO_2CH_2CO_2)$	286	(7.92)	1358	1.76			6, 7
	$Cu(CO_2CH_2CO_2) \cdot H_2O$	Room temp.	...	1530	(1.92)			158
	$Cu(CO_2CH_2CO_2) \cdot 2H_2O$	Room temp.	...	1680	(2.02)			158
	$Cu(CO_2CH_2CO_2) \cdot 3H_2O$	296	(6.89)	1598	1.95			7 (158)
Succinic acid	$Cu(CO_2(CH_2)_2CO_2)$	299	(4.20)	812	1.40			6, 7 (158)
	$Cu(CO_2(CH_2)_2CO_2) \cdot 2H_2O$	298	(3.41)	819	1.40			7
Glutaric acid	$Cu(CO_2(CH_2)_3CO_2)$	300	(4.09)	861	1.45			6, 7 (158)
Adipic acid	$Cu(CO_2(CH_2)_4CO_2)$	289	(3.32)	768	1.33			6, 7 (158)
Pimelic acid	$Cu(CO_2(CH_2)_5CO_2)$	291	(3.45)	853	1.41			6, 7 (158)
Suberic acid	$Cu(CO_2(CH_2)_6CO_2)$	288	(3.36)	897	1.44			6, 7 (158)
Azelaic acid	$Cu(CO_2(CH_2)_7CO_2)$	290	(3.01)	860	1.41			6, 7 (158)
Sebacic acid	$Cu(CO_2(CH_2)_8CO_2)$	288	(2.94)	900	1.44			6, 7 (158)
Camphoric acid	(structure)	Room temp.	...	945	(1.51)			158 (181)
	(structure) $\cdot 2.5H_2O$	Room temp.	...	918	(1.49)			158 (181)
α-Methyl-adipic acid	$Cu(CO_2CH(CH_3)(CH_2)_3CO_2)$	Room temp.	...	840	(1.43)			158 (181)
β-Methyl-adipic acid	$Cu(CO_2CH_2CH(CH_3) \cdot (CH_2)_2CO_2)$	Room temp.	...	825	(1.41)			158 (181)
Thioacetic acid	$Cu(CH_3COS)_2 \cdot (nH_2O?)$	...	...	...	0			151
Diazoamino-benzene	$Cu(C_6H_5N:NNC_6H_5)_2$	294	0.09	236	0			69, 72

[a] Compounds marked with superscript t.v. were measured for temperature variation of susceptibilities. [b] The values in parentheses are the calculated ones which were missed in original papers. [c] Different modification. [d] Different modification.
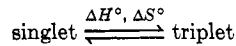
TABLE II

MAGNETIC PROPERTIES OF COPPER(II) COMPOUNDS CONTAINING MONATOMIC BRIDGES

Ligand	Formula of compounds[a]	T, °K.	$x_g \times 10^6$,[b] c.g.s., e.m.u.	$x_a \times 10^6$,[b] c.g.s., e.m.u.	μ,[b] B.M.	J cm.$^{-1}$	J kcal. mole^{-1}	References
	$CuO^{t.v.}$	300	3.033	254	0.78			155 (19, 23, 35, 77, 83, 108, 190)
	CuS	293	−0.03	(30)	(0.3)			108
	$CuSe$	293	−0.14	(30)	(0.3)			108
	$CuCl_2^{t.v.}$	293	9.25	1300	(1.75)			108 (19, 23, 35, 37, 167, 190)
	$CuCl_2 \cdot 2H_2O$	293	8.15	1475	(1.87)			108 (23, 35, 37, 155, 176, 177)
	$CsCuCl_3^{t.v.}$	290	4.71	1528	(1.89)			35
		300	...	...	1.95			43
	$KCuCl_3$	290	6.0	1332	(1.77)			35
	$CuBr_2^{t.v.}$	293	3.074	756	(1.31)			155 (77, 83, 108, 190)
	$CuF_2^{t.v.}$	293	10.0	1050	1.57			76 (20, 34)
		290	(8.54)	(889)	(1.44)			38
	$CuF_2 \cdot 2H_2O$	293	11.35	1600	1.94			152
	$KCuF_3^{t.v.}$	300	...	...	1.38			130 (133)
Pyridine N-oxide	$CuCl_2 \cdot C_5H_5NO^{t.v.}$	292	0.56	230	0.73			103
		293	...	...	0.77		2	71
		298	...	...	0.85			161

Table II (Continued)

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$,[b] c.g.s., e.m.u.	$\chi_a \times 10^6$,[b] c.g.s., e.m.u.	μ,[b] B.M.	J cm.^-1	J kcal. mole^-1	References
Pyridine N-oxide	CuCl₂·(C₅H₅NO)₂	292	−0.00	150	0.59			103
		298	...	...	0.63			161
Pyridine N-oxide, di-methylform-amide	CuCl₂·C₅H₅NO·(CH₃)₂NCOH	292	−0.08	120	0.53			103
Pyridine N-oxide, di-methyl sulfoxide	CuCl₂·C₅H₅NO·(CH₃)₂SO	292	−0.01	140	0.57			103
Dimethyl sulfoxide	CuCl₂·(CH₃)₂SO	292	7.56	1700	1.99			103
	CuCl₂·[(CH₃)₂SO]₂	292	4.58	1470	1.85			103
Pyridine N-oxide	CuBr₂·C₅H₅NO	292	0.0	120	0.53			103
		293	...	...	0.65			71
	CuBr₂·(C₅H₅NO)₂	292	1.80	915	1.46			103
Pyridine N-oxide, di-methylform-amide	CuBr₂·C₅H₅NO·(CH₃)₂NCOH	292	−0.18	95	0.47			103
Pyridine N-oxide, di-methyl sulfoxide	CuBr₂·C₅H₅NO·(CH₃)₂SO	292	0.93	535	1.12			103
Dimethyl sulfoxide	CuBr₂·[(CH₃)₂SO]₂	292	3.47	1480	1.86			103
Pyridine N-oxide	Cu(ClO₄)₂·(C₅H₅NO)₄	298	...	...	1.62			161
		293	...	...	2.09			71
3-Methylpyridine N-oxide	CuCl₂·CH₃C₅H₄NO	297	0.04	125	0.55			146
4-Methylpyridine N-oxide	CuCl₂·CH₃C₅H₄NO	298	0.00	113	0.52			146
2,4-Dimethylpyridine N-oxide	CuCl₂·(CH₃)₂C₅H₃NO	297	−0.39	21	0.22			146
Quinoline N-oxide	CuCl₂·C₉H₇NO	293	...	...	0.36			71
	CuBr₂·C₉H₇NO	293	...	...	0.40			71
4-Nitroquinoline N-oxide	CuCl₂·O₂NC₉H₆NO	297	4.70	1668	1.99			146
	CuCl₂·(O₂NC₉H₆NO)₂	299	2.57	1555	1.93			146
Triphenylarsine oxide	CuCl₂·[(C₆H₅)₃AsO]₂	299	(1.40)	1539	1.92			57
	CuBr₂·[(C₆H₅)₃AsO]₂	301	(0.603)	993	1.56			57
Triphenylphosphine oxide	CuCl₂·[(C₆H₅)₃PO]₂	299	(2.01)	1797	2.08			57
	CuBr₂·[(C₆H₅)₃PO]₂	300	(1.59)	1664	2.01			57
	Cu(CH₃CO₂)₂·(C₆H₅)₃PO	299	(1.55)	959	1.52			57
N,N-Dimethyl-acetamide	Cu(ClO₄)₂·[CH₃CON(CH₃)₂]₄·H₂O	300	(1.12)	1018	1.57			32
8-Hydroxy-quinoline	Cu·C₉H₆NO·Cl[t.v.]	298	(1.31)	318	0.87			41, 42
		293	...	...	1.14			70
	Cu·C₉H₆NO·Br	297	(1.77)	510	1.10			41, 42
	Cu·C₉H₆NO·NO₃·H₂O[t.v.]	296	...	...	1.39			70
	[Cu₂(C₉H₆NO)₃]ClO₄·0.5C₂H₅OH	295	...	...	1.60			70
N,N-Diethyl-N'-methyl-ethylene-diamine	{Cu₂[(C₂H₅)₂NCH₂CH₂NHCH₃]₂-(OH)₂}(ClO₄)₂[t.v.]	298	...	1271	1.69		1.07	74

$\Delta H° = 1.06$ kcal. mole^-1

singlet $\underset{\Delta H°, \Delta S°}{\rightleftharpoons}$ triplet

$\Delta S° = 2.2$ e.u.

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$,[b] c.g.s., e.m.u.	$\chi_a \times 10^6$,[b] c.g.s., e.m.u.	μ,[b] B.M.	J cm.^-1	J kcal. mole^-1	References
N,N,N',N'-Tetraethyl-ethylene-diamine	{Cu₂[(C₂H₅)₂NCH₂CH₂N(C₂H₅)₂]₂-(OH)₂}(ClO₄)₂[t.v.]	297	...	881	1.38		1.17	74

$\Delta H° = 1.49$ kcal. mole^-1

singlet $\underset{\Delta H°, \Delta S°}{\rightleftharpoons}$ triplet

$\Delta S° = 2.6$ e.u.

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$	$\chi_a \times 10^6$	μ			References
o-Toluic acid	Cu(CH₃C₆H₄CO₂)OH·0.5(CH₃C₆H₄CO₂H)	300	3.86	1221	1.72			17
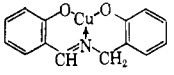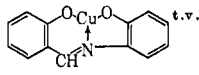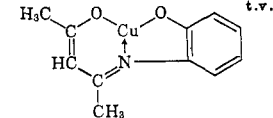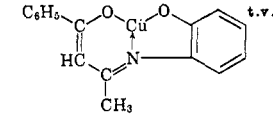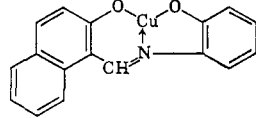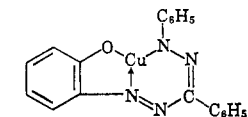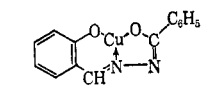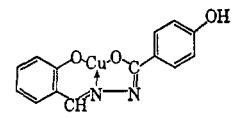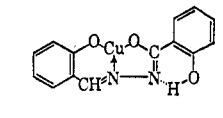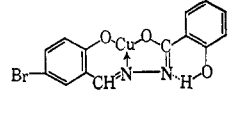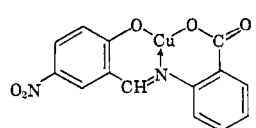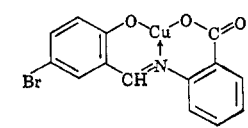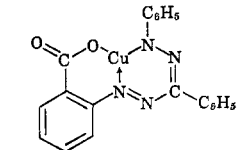
Table II (Continued)

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$,[b] c.g.s., e.m.u.	$\chi_a \times 10^6$,[b] c.g.s., e.m.u.	μ,[b] B.M.	J cm.$^{-1}$	J kcal. mole^{-1}	References
p-Toluic acid	$Cu(CH_3C_6H_4CO_2)OH \cdot 0.5(CH_3C_6H_4CO_2H)$	299	4.37	1366	1.82			17
Salicylal-o-hydroxy-benzylamine		287	0.705	330	0.87			104, 105
Salicylal-o-hydroxyanil		287	2.41	780	1.34	293	0.84	104, 105 (33) 10
Acetylacetone-mono(o-hy-droxyanil)		287	2.81	815	1.37	298	0.85	104, 105 10
Benzoylacetyl-acetone-mono(o-hy-droxyanil)		287	1.25	535	1.11	414	1.18	104, 105 10
2-Hydroxy-naphthalde-hyde-1-(2-hydroxyanil)		298	2.01	810	1.39			106, 107
2-Hydroxy-formazyl-benzene		298	1.83	870	1.44			106, 107
Salicylalde-hydebenzoyl-hydrazone		Room temp.	...	...	1.08			119
Salicylalde-hyde-p-hydroxy-benzoyl-hydrazone		Room temp.	...	...	1.02			119
Salicylalde-hyde-o-hydroxy-benzoyl-hydrazone		Room temp.	...	...	1.20			119
5-Bromosalicyl-aldehyde-o-hydroxy-benzoyl-hydrazone		Room temp.	...	...	1.20			119
5-Nitrosali-cylalanthra-nilic acid		298	3.81	1470	1.87			106, 107
5-Bromosali-cylalanthra-nilic acid		298	3.40	1460	1.87			106, 107
2-Carboxy-formazyl-benzene		298	2.94	1380	1.81			106, 107

TABLE II (Continued)

Ligand	Formula of compounds[a]	T, °K.	$\chi_g \times 10^6$,[b] c.g.s., e.m.u.	$\chi_a \times 10^6$,[b] c.g.s., e.m.u.	μ,[b] B.M.	$-J-$ cm.$^{-1}$	kcal. mole^{-1}	References
Salicylalde-hyde-2-mer-captoanil		301–304	...	...	1.82			145
2-Hydroxy-5-methylbenz-aldehyde-o-mercaptoanil		301–304	...	...	1.93			145
5-Bromosalicyl-aldehyde-o-mercaptoanil		301–304	...	...	1.76			145
o-Hydroxy-aceto-phenone		298	...	1085	(1.61)			33
Bis(salicylal)-1,7-hepta-methylene-diamine		298	...	1070	(1.60)			33
Bis(salicylalde-hyde)3,3'-diimino-di-n-propyl-amine		298	...	810	(1.39)			33
Bis(salicylal)-1,8-naphthyl-enediamine		298	...	1010	(1.56)			33
Salicylal-p-hydroxy-aniline		298	...	950	(1.51)			33
Benzamidoxime	Cu[C$_6$H$_5$C(NH$_2$):NO]OH	Room temp.	2.723	...	1.23			9
1,2,4-Triazole	CuCl$_2$	293	6.45	...	1.81			82
	CuSO$_4$ ·4H$_2$O	293	2.58	...	1.62			82
	Cu(C$_2$H$_2$N$_3$)$_2$[c]	293	3.9	...	1.4			82
	Cu(C$_2$H$_2$N$_3$)$_2$[c]	293	5.50	...	1.66			82

[a] Compounds for which temperature variation of susceptibilities were measured are marked with a superscript t.v. [b] The values in parentheses are the calculated ones which were missed in original papers. [c] Different modifications.
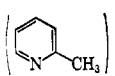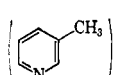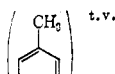
mechanism are possible, direct interaction and super-exchange interaction (cf. section III). However, this classification results in approximately the same group-ing of the compound as those in Table I and II.

Copper(II) formate yields a wide range of complexes, several anhydrous forms, and many solvated compounds. A large variation in magnetic properties is shown by this group of complexes; some are normal and others have subnormal moments. In the latter group, both mechanisms of magnetic interaction are found. Due to their unique behavior, the magnetic data of copper(II) formate complexes are presented separately in Table III.

The tables also contain the data of the compounds

Table III

Magnetic Data for Copper(II) Formate Complexes

Ligand	Formula of complexes[a]	T, °K	$\chi_g \times 10^6$, c.g.s., e.m.u.	$\chi_a \times 10^6$, c.g.s., e.m.u.	μ, B.M.	J^b cm.$^{-1}$	J^b kcal. mole^{-1}	References
Formic acid	Cu(HCO2)2[t.v.], royal blue	296	9.88	1566	1.90			135 (20)
	Cu(HCO2)2[t.v.], turquoise	291	8.52	1357	1.75			135 (20)
	Cu(HCO2)2[t.v.], blue	289	7.33	1174	1.61			134 (3, 135, 158)
	Cu(HCO2)2·2H2O[t.v.]	291	8.00	1591	1.90			135
	Cu(HCO2)2·4H2O[t.v.]	290	4.90	1200	1.67			99, (3, 134, 135)
	Cu(HCO2)2·(HCO2H)4	290	2.87	1173	1.61			135
Formic acid, aniline	Cu(HCO2)2·(C6H5NH2)2[t.v.]	296	3.87	1489	1.85			136
Formic acid, pyridine	Cu(HCO2)2·C5H5N[t.v.]	304	1.83	523	1.07			136
						632 (150)	1.81 (150)	136
						543 (250)	1.55 (250)	136
						550 (350)	1.57 (350)	136
Formic acid, α-picoline	Cu(HCO2)2·[2-methylpyridine][t.v.]	297	1.71	530	1.06			136
						614 (150)	1.75 (150)	136
						538 (250)	1.54 (250)	136
						538 (350)	1.54 (350)	136
Formic acid, β-picoline	Cu(HCO2)2·[3-methylpyridine][t.v.]	299	1.83	560	1.10			136
						538 (250)	1.54 (250)	136
						512 (350)	1.46 (350)	136
Formic acid, γ-picoline	Cu(HCO2)2·[4-methylpyridine][t.v.]	296	1.70	527	1.06			136
						701 (150)	2.00 (150)	136
						534 (250)	1.53 (250)	136
						546 (350)	1.56 (350)	136
Formic acid, dioxane	Cu(HCO2)2·0.5C4H8O2[t.v.]	290	1.92	453	0.96			136
						628 (150)	1.80 (150)	136
						558 (250)	1.60 (250)	136
						552 (350)	1.58 (350)	136
Formic acid, urea	Cu(HCO2)2·H2NCONH2	290	2.01	500	1.08			99, 102
	Cu(HCO2)2·(H2NCONH2)2·2H2O	290	3.46	1200	1.67			99, 102

[a] Compounds for which temperature variation of susceptibilities were measured are marked with a superscript t.v.   [b] Values in parentheses are in °K.

with normal moments which are considered to be important for comparative discussion.

The data are presented in a manner similar to that of Foëx (47), whose reference book was of invaluable assistance in the preparation of this review. When the effective magnetic moment, μ, was not given, the values were calculated by use of the formula, $\mu = 2.84(\chi_a T)^{1/2}$. χ_a is the magnetic susceptibility per copper(II) ion corrected for the diamagnetism of the other atoms in the compounds. If the missing value was to be calculated for a measurement at "room temperature," 300°K. was used in the above formula. The data for specific or mass susceptibility χ_g (susceptibility per gram) are also given in the tables.

It must also be kept in mind that some authors have calculated the effective magnetic moment with or without taking into account the temperature independent paramagnetism, $N\alpha$, or the diamagnetic correction for the copper(II) ion. Some have used the Pascal constants for the diamagnetic correction

of the nonmetal part of the molecule, and some have used the experimental values. Moreover, the numerical values of Pascal's constants are different in detail from table to table.

The J-value, the exchange integral, which corresponds to the separation between a singlet and a triplet state, is the important numerical value when discussing magnetic interaction. J-values are available for only a few compounds at present; those listed are obtained from $\chi_M–T$ curves. However, in many cases, even without J-values, the use of magnetic moments can lead to fruitful discussions and important conclusions.

In this review, the topics are restricted to the copper(II) compounds with subnormal magnetic moment at room temperature. No doubt many other copper(II) compounds have anomalous magnetic properties at low temperatures, but appear to be normal ($\mu \rightleftharpoons 1.73$ B.M.) at or near room temperature. In many cases the deviation from normal behavior at low temperatures is produced by mechanisms similar to those discussed

here. The compounds for which temperature variation of susceptibilities was measured are marked with t.v. in the tables. It is hoped that this review will be of interest and service even though these compounds may not be mentioned.

Reviews of copper(II) compounds with subnormal magnetic moments have been presented by several authors (8c, 44, 91a, 116, 117, 151, 191, 192).

Very recently Earnshaw (39a) has prepared chromous compounds with subnormal magnetic moments such as the oxalate (anhydrous and monohydrate), the anhydrous benzoate, and two forms of the anhydrous formates (blue, normal moment; red, subnormal moment). The measurements of the susceptibilities were made over a range of temperatures. The results for chromium(II) compounds are consistent with those for the corresponding copper(II) compounds (cf. the relative sections of the present paper). Such comparative study will be of great help to obtain a better understanding of the physico-chemical behaviors of these compounds because structural and magnetic similarities between the compounds of the d^4 chromium-(II) and the d^9 copper(II) ions are well established.

II. THE NATURE OF THE COPPER–COPPER BOND IN COPPER(II) ACETATE AND ITS HOMOLOGS

The studies on the copper(II) compounds with subnormal magnetic moment have been most extensive with copper(II) acetate and its homologs.

In 1915, Lifschitz and Rosenbohm (127) recorded that the molar susceptibility of copper(II) acetate monohydrate at room temperature is much lower than that usually observed for copper(II) compounds. Many investigators have repeated these magnetic measurements, and its abnormally low magnetic moment has been established (45).

In 1951, Guha (64) found that the magnetic susceptibility of its hydrate passes through a maximum at near 270°K. and decreases rapidly as the temperature is lowered, not obeying the Curie–Weiss law.

In 1951–1953, the anomalous behavior of its paramagnetic resonance spectrum was observed by many investigators (1, 27–29, 121, 125). The spectra resemble those of an ion of spin 1 rather than spin ¹/₂ which is present in most ordinary copper(II) compounds. Furthermore, the intensity decreases as the temperature is lowered in agreement with Guha's result of the temperature variation of susceptibilities. Bleaney (29) considered the isolate pairs of copper(II) ions must interact through exchange forces of Kramer's super-exchange type (4, 115).

In 1953, Niekerk and Schoenning (178, 179) determined the crystal structure of copper(II) acetate monohydrate. It consists of a binuclear molecule Cu_2(CH₃COO)₄·2H₂O in which copper(II) ions are bridged in pairs by four acetate groups with two water mole-
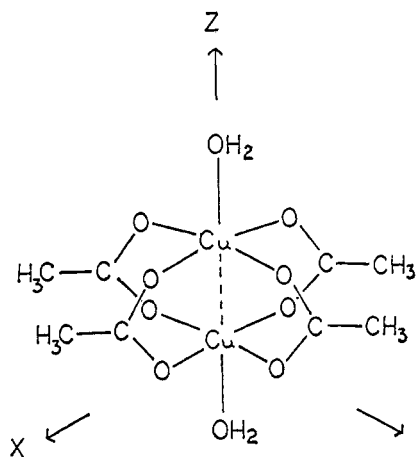
Fig. 1.—Schematic expression of the structure of Cu_2(CH₃COO)₄·2H₂O molecule.

cules occupying the terminal positions (Fig. 1). The copper(II) ion is 0.22 Å. out of the plane of the four oxygen atoms. The striking feature of this sixfold coordinated copper complex is the close approach of 2.64 Å. between the two copper(II) ions which is only slightly greater than 2.56 Å., the interatomic distance in metallic copper.

The recent determination of the structure of monopyridinecopper(II) acetate has revealed that this also has the same type of dimeric structure (12).

In 1956, exact measurements of the temperature variation of the magnetic susceptibilities of anhydrous and hydrated copper(II) acetates were performed by Figgis and Martin (45) and Perakis (155) for the pur-
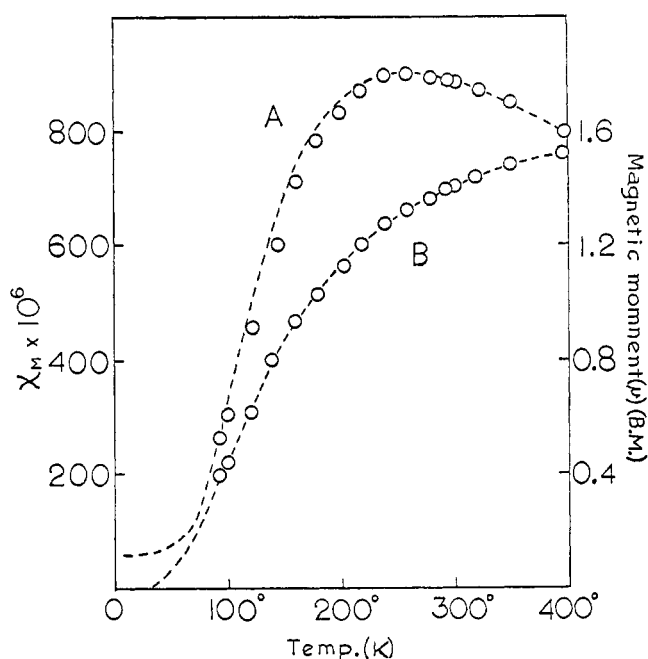

Fig. 2.—Magnetic susceptibilities (χ_M) and magnetic moments (μ) of copper(II) acetate monohydrate: - - - -, theoretical curves; curve A, magnetic susceptibilities; curve B, magnetic moments; O, experimental values.

pose of obtaining more information about the nature of the copper–copper bond in the acetates. Figgis and Martin's discussion will be described briefly in the following.

The molar susceptibility, χ_M, is expressed as

$$\chi_M = \frac{g^2 N \beta^2}{3kT} (1 + \frac{1}{3} e^{J/KT})^{-1} + N\alpha \qquad \text{(Eq. 1)}$$

where g is the magnetic field splitting factor which is 2 if the magnetic moment arises from spin only, J is the exchange integral of magnetism theory, and $N\alpha$ is the temperature-independent paramagnetism of 1 mole of copper(II) ions (8a, 29, 45). The curves of χ_M obtained by experiment coincide well with those based on Eq. 1 (cf. Fig. 2). It has a definite maximum at a certain temperature, an indication of the antiferromagnetism of the substance.

J-values were calculated by inserting the measured χ_M values into eq. 1; $J = 302$ cm.$^{-1}$ for anhydrous copper(II) acetate, 286 cm.$^{-1}$ for the monohydrate. The sign of J indicates that the molecular triplet state lies above the singlet ground state (antiferromagnetism). The distance between the two states corresponds to J. The energy level diagram of 3d orbitals of the copper(II) ion in $[Cu(H_2O)_6]^{2+}$ was given by Polder (160) (Fig. 3).
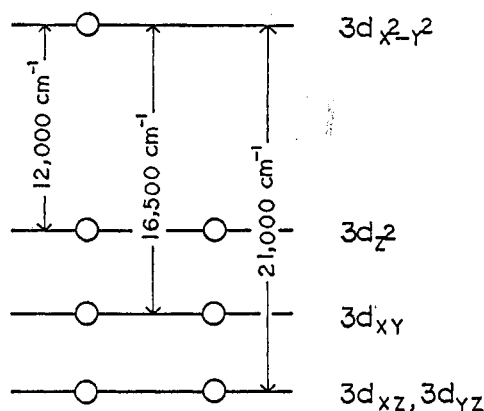

Fig. 3.—Energy level diagram of copper(II) ion in $[Cu(H_2O)_6]^{2+}$.

When the three axes of the Cartesian coordinates are defined as in Fig. 1, three types of bonds can occur between the copper(II) ions in the pair: σ (d_{z^2}–d_{z^2}), π (d_{xz}–d_{xz}, d_{yz}–d_{yz}), and δ (d_{xy}–d_{xy}, $d_{x^2-y^2}$–$d_{x^2-y^2}$). The overlap of the orbitals in these bondings decreases in the order $\sigma > \pi > \delta$ (45, 49). The bond type present is determined by two factors: (a) the energy levels of the orbitals used for bond formation and (b) the magnitude of the overlap of the orbitals. The possibility of occurrence of π-orbitals can be eliminated because the π-overlap is not large, and the orbitals for this interaction are present at the lowest level. The δ-bond between d_{xy} orbitals is also eliminated in a similar manner.

The $d_{x^2-y^2}$ level is the highest one and δ-bonding

between $d_{x^2-y^2}$ orbitals is most likely to occur. However, the magnitude of the overlap between $d_{x^2-y^2}$ orbitals is less than that between d_{z^2} orbitals which are below the $d_{x^2-y^2}$ orbitals. The bonding will then be determined by the competition in overlap between d_{z^2} and $d_{x^2-y^2}$ orbitals.

Figgis considered the promotion energy of an electron from $3d_{z^2}$ to $3d_{x^2-y^2}$ to be at least 12,000 cm.$^{-1}$. This is too large to allow the $3d_{z^2}$ orbitals to become available for σ-bonding. They proposed, therefore, a "very weak covalent δ-bond" between the two copper(II) ions (cf. Fig. 4). However, the δ-bond is considered
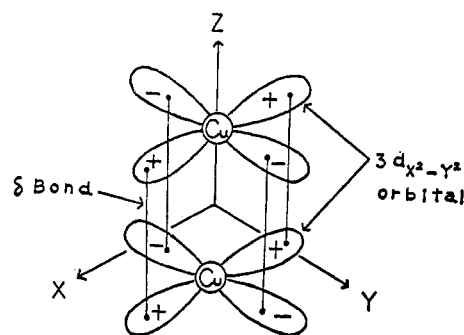

Fig. 4.—Schematic expression of the formation of a δ-bond between $3d_{x^2-y^2}$ orbitals in copper(II) acetate monohydrate.

to be so weak that the configuration of the binuclear molecule can be maintained only by the four bridging acetate groups.

Ross (164) re-examined the published paramagnetic resonance spectrum and pointed out that the experimental g-values can be explained only by δ (or δ') bond models, supporting Figgis and Martin's proposal.

Applying valence-bond theory to free-atom orbitals, Ross and Yates (165) calculated the J-value of δ ($3d_{x^2-y^2}$–$3d_{x^2-y^2}$) and σ ($3d_{z^2}$–$3d_{z^2}$) bonds in copper(II) acetate obtaining a value of 4 cm.$^{-1}$ for the δ-bond and 1600 cm.$^{-1}$ for the σ-bond, respectively. However, if the orbital expansion occurs under the influence of the ligand field by an amount corresponding to a reduction of 25% in the effective nuclear charge (Z_{eff}) from the value based on Slater's rules, the J-value of the δ-bond is increased to the experimental value of 300 cm.$^{-1}$. They also suggested that the mixing of a few per cent of σ-character in the δ-bond would result in the observed J-value.

The difficulty of a large orbital overlap between copper(II) ions is also inferred simply in the following way (184). The expansion of 3d orbitals of the metal ion of the first transition elements expected from Hartree approximation is: Mn^{2+} (0.80), Fe^{2+} (0.75), Co^{2+} (0.72), Ni^{2+} (0.69), Cu^+ (0.96), and Zn^{2+} (0.74) Å. Thus, the 3d expansion of the copper(II) ion is assumed to be less than 1 Å. From this, and from the ionic radius of the Ni^{2+} and Zn^{2+} ions, 0.74 and 0.83 Å., respectively, the ionic radius of the copper(II)

ion must be approximately 0.7 to 0.8 Å., much less than half of the copper–copper bond distance, 2.64 Å., in copper(II) acetate monohydrate. Such a small ionic radius is in agreement with that obtained from X-ray data of copper(II) compounds, such as $CuCl_2 \cdot 2H_2O$ (68).

Recently, Forster and Ballhausen treated the electronic structure of copper(II) acetate in terms of molecular orbital theory (49). The important point of their treatment lies in the assumption of a large overlap between $3d_{z^2}$ orbitals so that antibonding level of the $3d_{z^2}$ molecular orbitals has a higher energy than that of the molecular orbitals from $3d_{z^2-y^2}$. This then suggests a strong σ-bond ($3d_{z^2}$–$3d_{z^2}$) between copper(II) ions in the pair instead of the weak δ-bond proposed by Figgis (45, 165). In this treatment, the antiferromagnetism of copper(II) acetate is produced by the singlet → triplet transition, $^1A_{1g}$ → $^3B_{1g}$, corresponding to a one electron transition from the antibonding level of the $3d_{z^2-y^2}$ molecular orbitals to that of the $3d_{z^2}$ molecular orbitals, or vice versa. They succeeded in part to explain consistently the published data of the g-factors, the absorption bands in the visible and ultraviolet regions, and the antiferromagnetism. However, they emphasized that the proposed molecular orbital treatment is tentative.

Boudreaux (31) has reconsidered this problem in terms of the molecular orbital viewpoint very similarly to Forster and Ballhausen (49), but with an important difference in the order of the splitting of the d^9 configuration which comes from the different symmetry of half of the dimeric molecule, $H_2O \cdot (CH_3CO_2)_2Cu$. The orders proposed by the former and latter authors are $3d_{z^2-y^2} > 3d_{z^2} > 3d_{zz}, 3d_{yz} > 3d_{xy}$ for a square pyramidal symmetry (C_{4v}) and $3d_{z^2-y^2} > 3d_{z^2} > 3d_{xy} > 3d_{zz}, 3d_{yz}$ for a square planar (D_{4h}) distorted toward square pyramidal symmetry (C_{4v}), respectively. Boudreaux used in his calculations a numerical value of 6.3 for the effective nuclear charge, Z_{eff}, suggested by Ross and Yates (165). Again it was shown that for the copper–copper bond a δ-bond is more favorable than a σ-bond.

The complete explanation of the nature of the copper–copper bond is still an interesting unsolved problem.

III. Classification of Copper-to-Copper Magnetic Interaction

The copper(II) compounds with subnormal magnetic moments can be classified into the following two classes on the basis of the magnetic interaction.

A. DIRECT INTERACTION

Copper(II) acetate monohydrate, the structure of which has been determined (177, 178), is representative of this class in which copper-to-copper magnetic interaction is due to a direct bond between the copper(II) ions. Either from the valence-bond treatment or

from the molecular orbital treatment, the lower magnetic moment is deduced from the stronger copper-to-copper direct linkage (49, 164). All of the compounds listed in Table I belong in this category.

B. SUPER-EXCHANGE INTERACTION

In these compounds copper-to-copper interaction is due to the so-called "super-exchange interaction" (4, 114) among copper(II) ions. Most of the compounds belonging to this class contain monatomic bridges, in most cases an oxygen atom, joining copper(II) ions. Acetylacetone-mono(o-hydroxyanil)copper(II), the structure of which has recently been elucidated (10), is a typical example of this class. Compounds of this class are given in Table II except for some copper(II) formates (in Table III) which are considered to belong to this class.

However, these compounds with subnormal magnetic moments could possess some of both types of magnetic interactions. Martin (135) suggested that the subnormal magnetic moment of copper(II) formate tetrahydrate, the structure of which has been completely elucidated by X-ray analysis (98) (Fig. 5), is
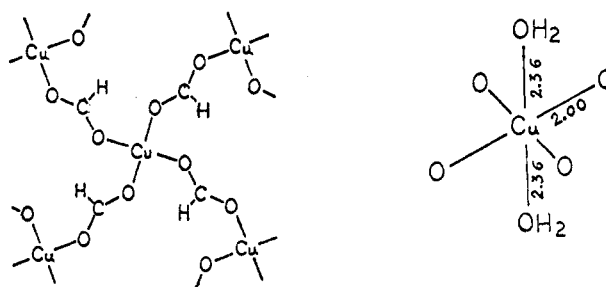

Fig. 5.—The structure of copper(II) formate tetrahydrate; one layer of $[Cu(HCOO)_2]_n$ is given: Cu–Cu = 5.80 Å., μ = 1.64 B.M.

primarily due to the super-exchange through a π-pathway set up by using $3d_{yz}$ or $3d_{zz}$ orbitals of the copper ion and of $2p_\pi$ orbitals of the bridging $HCOO^-$ radicals (cf. also section VC). In a similar manner, a π-pathway can be set up using the $3d_{xy}$ orbital of the copper(II) ion and $2p_\pi$ orbitals of COO^- ion in the copper(II) alkanoates having the dimeric structure. Watanabe (183) proposed the super-exchange interaction through the carboxylate ion as one of the possible interaction mechanisms. Forster and Ballhausen (49) also mentioned the possibility of "super-exchange" interaction in addition to the direct copper-to-copper interaction.

IV. Copper(II) Compounds with Direct Copper-to-Copper Interaction

The compounds most investigated which belong to this category are the salts of carboxylic acids with the exception of bis(diazoaminobenzene)copper(II) (69, 72). Most of them contain a dimer structure; but

some of them appear as compounds containing a poly-nuclear structure, such as the copper salts of α,ω-dicarboxylic acids (6, 7), hemiurea (79, 99), or dioxane addition compounds of some of the copper alkanoates (136). However, although these compounds show no unusual magnetic character, compared to many copper carboxylates with a dimer structure, they will also be discussed here.

A. FACTORS WHICH CONTROL THE DIRECT INTERACTION

If the magnetic interaction of copper(II) carboxylates originates from the direct metal-to-metal linkage, the interaction is expected to be affected by the distance between the metal ions. The magnetic interaction between metals is postulated to become larger as the metal distance becomes shorter. Copper(II) acetate monohydrate has a dimer structure in which the copper–copper distance is unusually short, 2.64 Å., leading to a fairly large magnetic interaction between copper(II) ions (1.43 B.M.). A very large magnetic interaction between metal ions is also present in chromous acetate which is isostructural with copper(II) acetate. The chromium–chromium distance is 2.64 Å., leading to diamagnetism (97, 179, 180).

The magnetic moment of pale blue copper salicylate tetrahydrate is 1.92 B.M. (78), in conformity with the large copper–copper distance, 3.728 Å. (67). On the other hand, the blue-green form has a moment of 1.45 B.M. (78). At present, its structure has not yet been elucidated. However, it is proposed that this compound has a copper–copper distance close to 2.64 Å., found in copper(II) acetate monohydrate (cf. section IVF).

The magnetic interaction is also affected by the nature of the attached ligand. The magnetic interaction will become larger as the ligand supplies more electron density to the central metal ion. The greater electron transfer makes the metal orbitals larger and results in a larger overlap. It should be noted that this type of promotion of magnetic interaction may be brought about not only by the four ligands (X) at the corners of square-planar configuration containing the copper(II) ion, but also by the terminal molecules (Y) in Fig. 6, giving an effective coordination number of six around each copper(II) ion.
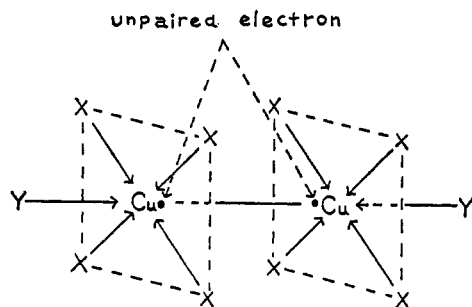

Fig. 6.—Configuration of copper(II) ions in the alkanoates.

Magnetic susceptibilities of the copper(II) salts of chloroacetic acids have been measured (113). The results obtained showed a good parallel between the pK values of the acids and the magnetic moments of the copper(II) salts (Table IV). Since the pK value of the acids can be taken as a measure of the electron-donation power of the carboxylate ions to the metal ion, it may be concluded that the larger electron donation to the metal ions results in larger magnetic interaction if the dimer structure is maintained.

The same parallelism can also be seen in Table V for

TABLE IV
pK Values and Magnetic Moments

Acids	pK of HL[a]	μ, B.M.[b]
CH_3COOH	4.6	1.39
$ClCH_2COOH$	2.6–2.9	1.42
$Cl_2CHCOOH$	1.25	1.66
Cl_3CCOOH	0.66	1.77
F_3CCOOH	0.23	1.9[c]

[a] HL means the acid after Bjerrum, et al. (24); see also ref. 2.
[b] The values in this column are those for anhydrous salts.   [c] Ref. 89.

TABLE V
pK Values and Magnetic Moments

Acids	pK of HL[a]	μ, B.M.[b]
o-Bromobenzoic acid	2.93	—
m-Bromobenzoic acid	3.87	1.73
p-Bromobenzoic acid	4.08	1.57
o-Toluic acid	3.92	1.61
m-Toluic acid	4.25	1.52
p-Toluic acid	4.35	1.51
o-Nitrobenzoic acid	2.21	1.64 (6H_2O)
m-Nitrobenzoic acid	3.47	2.05 (1H_2O)
p-Nitrobenzoic acid	3.40	1.56 (2H_2O)
Acetic acid	~4.75	1.39
Phenylacetic acid	4.28	1.44
Diphenylacetic acid	3.94	1.38

[a] See corresponding footnote in Table IV.   [b] Magnetic moments for anhydrous salts except nitrobenzoates where the water content is indicated in parentheses.

the copper(II) salts of monosubstituted benzoic acids with the exception of the copper(II) salt of m-nitrobenzoic acid (158). However, the observed irregularity is not unusual in this case because the copper salts of the three isomers of nitrobenzoic acid have different water content, which may lead in some of them to a structure different from the dimeric one (see section IVF).

The copper(II) salt of phenylacetic acid has a larger magnetic moment than copper(II) acetate in conformity with its smaller pK value. However, contrary to expectation, copper(II) diphenylacetate has a magnetic moment smaller than that of copper(II) phenylacetate even though the former has a smaller pK value (114) (see Table V). This type of irregularity has not been explained at present.

Another typical exception is copper(II) thioacetate. The pK value of thioacetic acid is 3.33, which is smaller than 4.75, that of acetic acid. Nevertheless, the magnetic measurement by Nyholm (151) showed that copper(II) thioacetate is nearly diamagnetic. One of the possible explanations is that the highly-polarizable sulfur atoms supply a large amount of electron density to the copper(II) ions which leads to a large magnetic interaction between them (151). This type of unusual electron transfer does not occur in the pure σ-bonds formed by the hydrogen ion which are responsible for the pK value of the acid.

All these examples pertain to the coordinate bonds at the four corners of the square containing the copper-(II) ion in its center. The same promotion effect in magnetic interaction will be produced by the bonds

found only in compounds with copper(II) and chromium(II) ions (178–180), both of which have an odd number of electrons in the e$_g$ orbitals, which leads to the Jahn–Teller distortion (49, 54, 154a). This seems to indicate that one of the conditions necessary for the formation of the dimeric structure is the easy removal of one of the ligands which are bound by weaker bonds in a distorted octahedral complex ion (L in Eq. 2). The formation of the dimeric structure is much more favorable in organic solvents than in water; it is destroyed in water, forming monomeric hydrated ions. This destruction of the dimeric structure can be avoided in organic solvents such as alcohol, ether, etc., which are ligands of coordinating power much weaker than the water molecule. If the formation reaction proceeds in the following way

L = solvent molecule
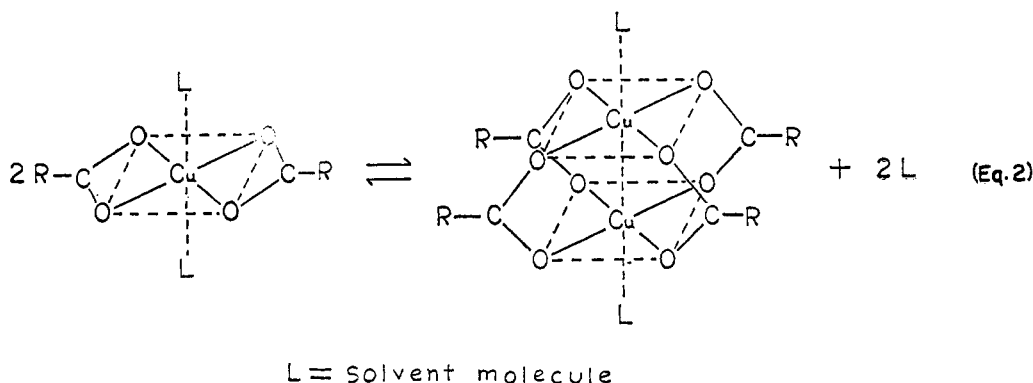
formed at the terminal positions marked by Y in Fig. 6. Martin (136) prepared some addition compounds of copper(II) formate with picolines, which are postulated to have the same dimeric structure as copper(II) acetate. Here, the same parallelism can be observed between the pK values of protonated picolines and the measured magnetic moments of the copper compounds (see Table VI).

TABLE VI
pK VALUES AND MAGNETIC MOMENTS

Bases	pK of H$^+$L^a	μ of addition compounds of copper(II) formate with picolines, B.M.
α-Picoline	6.20	1.06
β-Picoline	5.52	1.10
γ-Picoline	6.26–6.08	1.06

^{a} H$^+$L represents the protonated base after Bjerrum (24).

B. FACTORS CONTROLLING THE FORMATION OF DIMERIC MOLECULES IN SOLUTION

The dimerization reaction in solution is extremely complicated, and it is difficult to draw many conclusions at this time. However, several factors which seem to control the formation of the dimeric structure of copper-(II) carboxylates in solution can be discerned. The dimeric structure of a copper(II) acetate type has been

the system will gain entropy on the right side of the equation because the total number of molecules on the right side is greater than that on the left side (132b). This also may be one of the reasons why the dimeric structure can be retained in such solutions, although the bonds between the copper(II) and carboxylate ions are supposed to be rather weak.

However, Forster and Ballhausen (49) postulated that the dimeric complex was stabilized because of the large overlap of the 3d$_{z^2}$ orbitals between the pair of copper(II) ions in the complex.

Tsuchida (170, 173, 195) found from absorption spectra that of the three bromo- and three chloroacetates only copper(II) trichloroacetate does not appear as a dimeric molecule in dioxane; this may be due to the accumulation of the inductive effect of the many highly electronegative chlorine atoms. This seems to indicate that the stronger the coordinate bonds with the carboxylate ions the greater is the tendency for the formation of the dimeric structure in solution (cf. also section IVC). Tsuchida (171) also observed that those copper(II) carboxylates, which have the higher frequencies of the copper absorption band, have the greater tendency to form the dimeric structure in solution. The frequency of the absorption band can be taken as a measure of the strength of

the ligand field or the degree of covalency of the bonds (86, 91, 123, 154b). It, thus, can be concluded that a chemical bond of a definite strength is required to maintain a dimeric structure in solution. Such tendency for the formation of the dimeric molecule in solution parallels the fact that stronger coordinate bonds in dimeric molecules of copper(II) carboxylates produce larger magnetic interaction (cf. section IVA).

C. SOLVENT EFFECT

The solvent effect has been studied for copper(II) alkanoates. Two types of solvent effects should be distinguished: the effect on the formation of the dimeric molecules in solution and the effect on the magnetic interaction between copper(II) ions in the dimeric molecules.

In order to distinguish between these two effects, very accurate quantitative experiments are required. Information must be obtained about the concentration of dimeric molecules in a solvent and the magnetic moments of both the monomeric and dimeric molecules in the same solvent. No such work has appeared in the literature up to this time.

However, a fairly good correlation between the physical properties of solvents and the solvent effect has been shown to exist. The solvents which strengthen the coordinate bonds in copper(II) carboxylates promote both phenomena, the formation of dimeric molecules in solution and the magnetic interaction between copper(II) ions.

The methods by which these effects were studied are measurements of magnetic susceptibilities (113), of absorption spectra (62, 137, 171, 195), and actual isolation of the compounds in the dimeric state from solvents (171, 195). From these data the following solvent series results (the figures in parentheses are the dielectric constants of the solvents).

water, pyridine < methanol < ethanol, acetone, chloroform,
 (78)   (12)   (32)   (24)   (20)   (4.8)
    benzene < carbon tetrachloride, dioxane < ethyl ether
     (2.2)   (2.2)   (2.2)   (4.3)
——→

(The direction in which the formation of dimeric molecules or magnetic interaction becomes more prominent.)

This solvent series can be discussed in terms of two factors: (a) the dielectric constant of the solvent and (b) the coordination power of the solvent to the metal or complex ion.

The bonds between the carboxylate and the copper(II) ions are strengthened as the dielectric constant of the solvent decreases. Such tendency is indicated by the fact that the pK values of many chelate compounds recorded for aqueous organic solutions increase as the water content decreases (24). A stronger bond will correspond to greater covalency and greater covalency will result in a greater tendency to form the di-

meric molecules which in turn will result in greater magnetic interaction (cf. sections IVA and B).

This can be discussed best as it applies, for example, to the dimeric copper(II) acetate. The terminal position of the dimeric molecule (marked Y in Fig. 6) can be occupied by a solvent molecule. If the dimeric structure is not disturbed in solution, the stronger coordinate bond at the terminal position will produce stronger magnetic interaction between the copper(II) ions (cf. section IVA). Solvent molecules with strong coordination power, however, may replace the metal carboxylate's oxygen bonds and lead to the breakdown of the dimeric structure. Whether in a particular solvent the dimeric structure is maintained, is determined by the bonding competition between the carboxylate ions and the solvent molecules.

The order of solvent effect coincides with the order of dielectric constants indicating that its influence is a most important factor. In water, the dimeric structure is destroyed and copper(II) ions are present in a hydrated or partly hydrated form (59, 194). Pyridine destroys the dimeric structure because of its strong coordination power despite its lower dielectric constant (113). The dielectric constants of ethanol and acetone, although much larger than those of chloroform and benzene, seem to have the same degree of solvent effect. They should be less effective from the point of view of dielectric constant, however, at the same time should be more effective as far as coordination power is concerned (26, 51, 80, 94, 95).

The dielectric constants of benzene and dioxane are nearly the same, and the solvent effects of these two compounds, therefore, should also be the same. However, dioxane is found to be more effective than benzene because of its greater coordination power (136, 139, 147). It is not clear at present why carbon tetrachloride and dioxane, with nearly the same dielectric constant, show the same level of solvent effect in spite of their great difference in coordination power.

Dioxane is at least four times more basic toward ferric chloride than n-butyl ether (138), and n-butyl ether coordinates to metal ions more strongly than ethyl ether because of the greater inductive effect of the longer alkyl group. The dielectric constant of dioxane, however, is smaller than that of ethyl ether; both these factors should lead to a solvent effect of dioxane which is larger than that of ethyl ether. However, the reverse order is actually found. Tsuchida (171, 195) obtained the solvent order, dioxane < ethyl ether, as indicated by the fact that copper(II) trichloro- and trifluoroacetates do not show the 375-mμ band in dioxane but do so in ethyl ether. Furthermore, both compounds are obtained as crystals of the dimeric molecule on recrystallization from ethyl ether, but only as monomeric crystals from dioxane.

If the bond of the carboxylate ion to the metal ion

becomes very weak, it can then be replaced by solvent molecules with larger coordination power. The substitution of hydrogen atoms on acetic acid by atoms of the very electronegative halogens will decrease the coordination tendency of the carboxylate ion to the metal ion, leading to the breakdown of the dimeric structure in a strongly coordinating solvent. The coordination power of dioxane may be too strong to preserve the dimeric structure of copper(II) trichloro- or trifluoroacetate. On the other hand, the coordination power of ethyl ether is much smaller, and it cannot break up the dimeric structure.

It is suggested that a similar order of solvent effect is found for the absorption spectra of many monomeric copper(II) complexes: pyridine > methanol > chloroform, benzene > carbon tetrachloride. However, this order could be correlated only to the coordination power of the solvent (185).

More studies are necessary for a full understanding of the solvent effect in these systems.

### D. ABSORPTION SPECTRA IN THE VISIBLE AND ULTRAVIOLET REGIONS

The ultraviolet and visible spectra of a large number of copper(II) alkanoates and their derivatives have been measured in organic solvents and on single crystals of the salts (62, 135, 137, 169–173, 193–195). These studies reveal that these complexes have a new band at about 375 mμ both in solution and in the crystal. It was also shown that copper(II) benzoate and its derivatives, methyl-, chloro-, nitro-, and hydroxybenzoates have a band at 375–400 mμ in dioxane (17, 174).

The polarized absorption spectra of a few complexes have shown that three bands at about 300, 375, and 700 mμ are present when a direct copper-to-copper interaction exists in the complexes (169, 172, 193, 194) (cf.

Fig. 7.—Absorption spectra of copper(II) acetate monohydrate in the crystalline state (left scale, ———): ‖ absorption with the light polarized in the complex plane, ⊥ absorption with the light polarized along copper–copper linkage. Absorption in ethanol (right scale, - - - - -).

Fig. 7). The 700-mμ band was assigned to the normal metal–ligand interaction (49, 169, 193), the so-called copper band (25, 50).

Yamada (193) assumed that the 300-mμ band is due to the coordinated acetate groups. Forster and Ballhausen (49) did not discuss this band as its origin is unknown.

In organic solvents, the 300-mμ band disappeared, and a band was observed at about 250 mμ (193, 194). Graddon (62) assigned this band to a charge-transfer band of the type

$$RCOO^- + Cu^{2+} \rightarrow RCOO + Cu^+$$
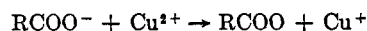
This was based on the fact that unlike the ligand-field band, no significant solvent effect was observed for this band.

Tsuchida (169, 193) assumed the band at 375 mμ to be due to the copper-to-copper linkage, based on the fact that it is a new band which is not seen in most copper(II) complexes. Furthermore, polarized absorption spectra show that the absorption at 375 mμ is much stronger along the copper-to-copper bond than in the plane of the complex.

The 375-mμ band was not observed for crystals of copper(II) formate tetrahydrate in which no direct copper-to-copper link exists (98, 169, 193). However, this band shows up again in dioxane solution in which copper(II) formate has a magnetic moment of 1.01 B.M., unusually low compared to that of most alkanoates (137).

The absorption spectra of copper(II) halogenoacetates were measured both in solution and in the solid (170, 171, 173, 195). A rough correlation is observed between the existence of the 375-mμ band and the magnetic moments of copper(II) chloroacetates (114, 173, 195). Copper(II) trichloroacetate tetrahydrate has no band at 375 mμ and its magnetic moment is normal.

The same correlation is also found between the magnetic moment of the various solutions of the alkanoates and the presence of the 375-mμ band. When copper(II) alkanoates with subnormal magnetic moment are dissolved in highly coordinating solvents, the 375-mμ band is not present and the magnetic moment of the solution is normal. If a poorly coordinating solvent is employed, the moment remains at a subnormal value and the 375-mμ band is present (113, 137, 169, 193, 194). Cryoscopic, distribution, and spectroscopic studies have also shown that the dimeric structure of copper(II) alkanoates persists in organic solvents (59, 61, 62, 137). Cryoscopic and ebullioscopic determinations together with magnetic measurements have also shown that the copper(II) complex of diazoaminobenzene exists as a diamagnetic dimer in benzene (69, 72).

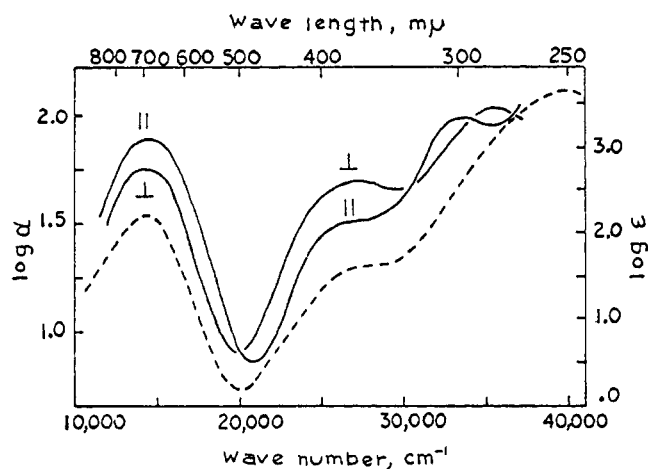The spectra of the copper(II) alkanoates have been found to be very similar to that of the copper(II) β-

diketones (60, 62). The 375-mμ band appears in both spectra. Graddon tentatively assigned the bands at 700 and 375 mμ to the $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transitions, respectively, on the basis of the polarization of the absorption bands observed by Yamada (169, 173). If the cause of the visible and near-ultraviolet bands of copper(II) alkanoates and copper(II) β-diketones is the same, the recent work by Basu (15) indicates the band at 375 mμ may be due to a ligand transition rather than a d–d transition.

The cause of the bands at 700 and 375 mμ in copper(II) acetate has also been considered theoretically (49, 164). However, the conclusions by different authors are not in agreement with each other. The electronic transitions deduced from the molecular orbital theory are postulated to occur through the d_{z^2} orbital rather than the $d_{x^2-y^2}$ orbital (49). It has also been suggested that the band at 700 mμ corresponds to the usual copper band (25), $i.e.$, a transition within half of the dimeric molecule. The band at 375 mμ is most likely due to the electronic configuration of the whole molecule (49).

However, it is believed at the present time that the appearance of a band at about 375 mμ does not prove the existence of a direct copper-to-copper interaction since many copper(II) compounds, whose structures are considered to be monomeric, have a band in this region (15, 60, 126)

The band of direct electronic transition between the singlet and triplet state separated by J, which should appear in the infrared region, has as yet not been observed.

More experimental and theoretical studies are necessary for these band assignments.

E. INFRARED ABSORPTION SPECTRA

Tsuchida (172, 194) found that sodium acetate and copper(II) formate, which has no dimeric structure, show a broad and strong antisymmetric COO$^-$ stretching absorption band between 1560 and 1600 cm.$^{-1}$. On the other hand, many of the dimeric copper(II) alkanoates show a rather sharp and well defined absorption band at 1595 to 1600 cm.$^{-1}$. They proposed that the observed different features in the infrared spectra are due to the difference in the state of the carboxylate ions; they considered this difference to be one of the evidences of binuclear structure.

Ploquin (158, 159) measured the magnetic moments for a series of copper(II) salts of α,ω-dicarboxylic acids

$$\text{HOOC(CH}_2)_{n-2}\text{COOH} \quad (n = 2\text{–}10)$$

Recently, Asai (6, 7, 118) carefully re-examined the magnetic moments of the same series of compounds and tried to correlate the obtained moments with the probable structure of the copper(II) salts (cf. Fig. 8). In view of the coplanarity of the oxalate radical and the
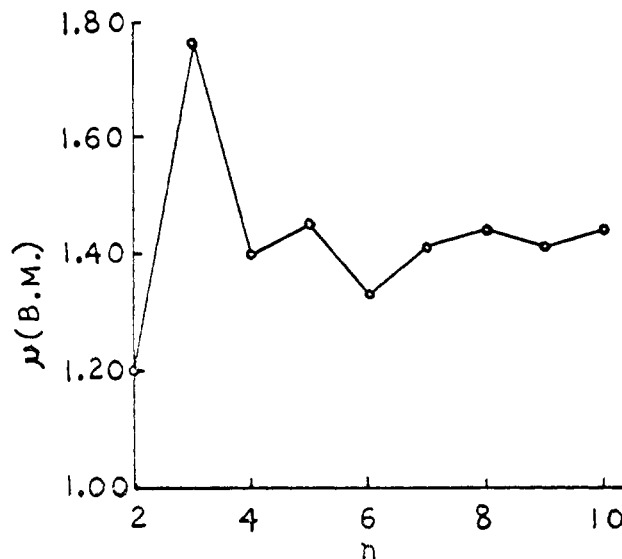

Fig. 8.—Dependence of the effective magnetic moment per one copper atom of the anhydrous copper(II) salts of α,ω-dicarboxylic acids, HOOC(CH$_2$)$_{n-2}$COOH.

observed subnormal magnetic moments, they suggested an infinitely extending two-dimensional network as the only conceivable structure. A remarkable exception is copper(II) malonate with a normal magnetic moment of 1.76 B.M., for which the same type of network structure is impossible.

A recent study of the electron spin resonance of some copper(II) salts of dicarboxylic acids (162) has shown that these salts do not show the resonance at 3.1 cm. which indicates pairing of copper(II) ions. This resonance, however, is observed for copper(II) malonate, supporting the conclusion made by Asai.

Kuroda (118, 124) recorded the infrared absorption for the same series of copper(II) compounds together with the corresponding sodium salts (Table VII). She found that the antisymmetric COO$^-$ stretching frequencies of these copper(II) compounds, with the single exception of copper(II) malonate, are shifted to higher frequencies compared to the bands of corresponding sodium salts. Furthermore, the plot of

TABLE VII

ANTISYMMETRIC COO$^-$ STRETCHING FREQUENCIES OF THE COPPER(II) α,ω-DICARBOXYLATES, Cu(CH$_2$)$_{n-2}$(COO)$_2$, AND THE CORRESPONDING SODIUM SALTS, AND THE MAGNETIC MOMENTS OF THE COPPER(II) SALTS

| | Stretching frequency, cm.$^{-1}$ | | | Magnetic moments, |
n	Cu salt	Na salt	Difference	μ
2	1665	1635	30	1.20
3	1595	1595	0	1.76
4	1608	1567	41	1.40
5	1590	1583	7	1.45
6	1582	1567	15	1.33
7	1592	1565	27	1.41
8	1595	1559	36	1.44
9	1595	1566	29	1.41
10	1595	1564	31	1.44

the difference between the COO$^-$ frequencies of the copper(II) and sodium salts, which is practically zero for copper(II) malonate with normal magnetic moment, against the number of carbon atoms in an acid radical, showed a fairly close resemblance in shape to that of the magnetic moment of the copper(II) salts plotted against the same abscissa.

Kuroda (122) measured the infrared absorption spectra of copper(II) alkanoates in a solid state and in dioxane (cf. Table VIII). The same tendency of

TABLE VIII
ANTISYMMETRIC COO$^-$ STRETCHING FREQUENCIES OF COPPER(II) ALKANOATES, $(C_nH_{2n+1}CO_2)_2Cu$ $(n = 0-9)$ AND THE MAGNETIC MOMENTS OF THE COPPER(II) SALTS

		Solid		In dioxane	
n	Compounds	ν_a (COO), cm.$^{-1}$	μ, B.M.	ν_a (COO), cm.$^{-1}$	μ, B.M.
0	$Cu(HCO_2)_2 \cdot 4H_2O$	1562	1.64	1636	1.01
0	$Cu(HCO_2)_2$	1565	1.61	Insoluble	
1	$Cu(CH_3CO_2)_2 \cdot H_2O$	1602	1.40	1624	1.36
1	$Cu(CH_3CO_2)_2$	1590	1.39		
2	$Cu(C_2H_5CO_2)_2$	1589	1.36	1620	1.26
3	$Cu(C_3H_7CO_2)_2$	1589	1.37	1620	1.25
4	$Cu(C_4H_9CO_2)_2$	1588	1.41	1620	1.26
5	$Cu(C_5H_{11}CO_2)_2$	1588	1.40	1620	—
6	$Cu(C_6H_{13}CO_2)_2$	1588	1.41	1620	—
7	$Cu(C_7H_{15}CO_2)_2$	1588	1.39	1620	—
8	$Cu(C_8H_{17}CO_2)_2$	1588	1.41	1620	—
9	$Cu(C_9H_{19}CO_2)_2$	1588	1.41	1620	—

band shift of the antisymmetric COO$^-$ stretching frequencies to higher frequencies was observed for these copper(II) compounds (58). The antisymmetric COO$^-$ band of copper(II) formate shows a remarkable shift from 1562 cm.$^{-1}$ in the solid state to 1636 cm.$^{-1}$ in dioxane, paralleling the large change of its magnetic moment from 1.64 B.M. in the solid state to 1.01 B.M. in dioxane. Since the antisymmetric COO$^-$ stretching frequency is known to be sensitive to the electronic environment of a carboxylate ion (92), one of the reasons for the observed band shift was believed to be the dimeric structure of the copper(II) salts, as opposed to the monomeric nature of the sodium salts. The author proposed that the electronic structure about the copper(II) ion or pair of copper(II) ions causes the lowering of the magnetic moments and the band shift.

The possibility of super-exchange interaction through the carboxylate groups is also pointed out, although the correlation between super-exchange interaction and the observed band shift is not clear at present (cf. section III).

F. PREPARATIVE VARIATIONS OF COPPER(II) CARBOXYLATES WITH SUBNORMAL MAGNETIC MOMENTS

The magnetic moment of copper(II) salicylate tetrahydrate obtained by Ploquin (158) is 1.44 B.M., indicative of a dimeric structure. However, the recent X-ray analysis of this compound by Hanic (67) has
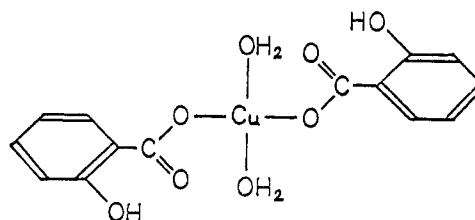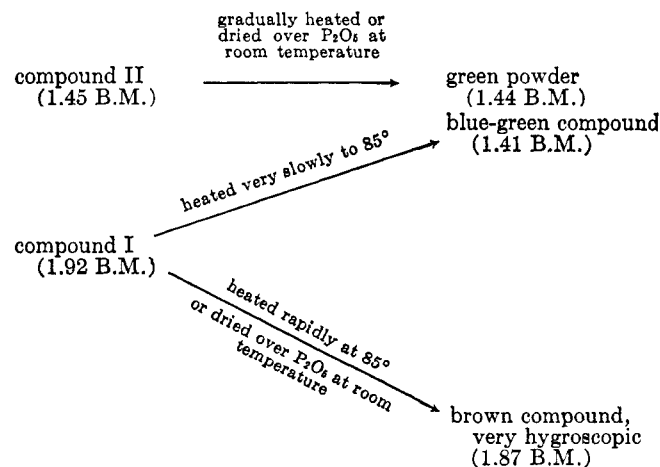

Fig. 9.—The structure of copper(II) salicylate tetrahydrate.

shown a monomeric structure given schematically in Fig. 9. The distance between the nearest copper(II) ions is 3.728 Å. The magnetic moment of this compound should be normal, based on the detailed structure. These two facts seem to be in conflict with each other. Inoue (78) has prepared the copper(II) salicylate tetrahydrate(I) by the same method as employed by Hanic and measured the magnetic susceptibility. The compound, pale blue needles, showed a moment of 1.92 B.M. in conformance with the monomeric structure indicated by X-ray analysis. The compound prepared by Ploquin must be a modification of compound I. In fact, Inoue has succeeded in preparing the compound II, blue-green plates, with a subnormal magnetic moment, 1.45 B.M. The preparation method used is given schematically as
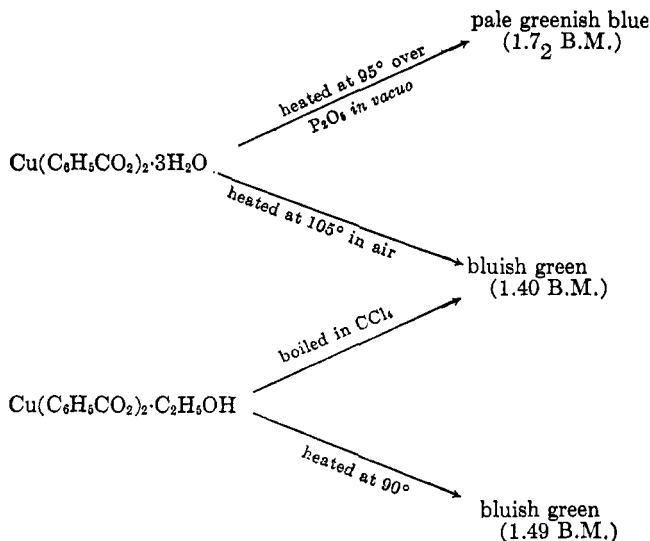
I + equimolar salicylic acid
(in a small amount of ethanol containing a small amount of water)

cool to 0°
→ tetrahydrate II

ethanol solution of salicylic acid + aqueous solution of copper (II) acetate

cool
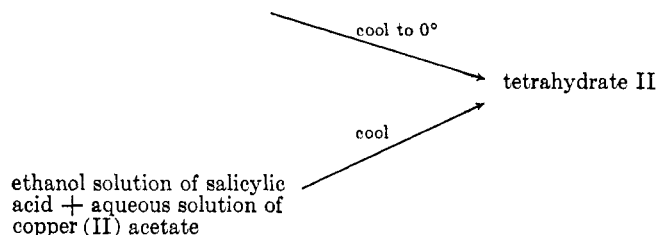
Compound II is easily converted to I by recrystallizing II from water. They also succeeded to prepare some anhydrous modifications with a variety of magnetic moments as shown below.
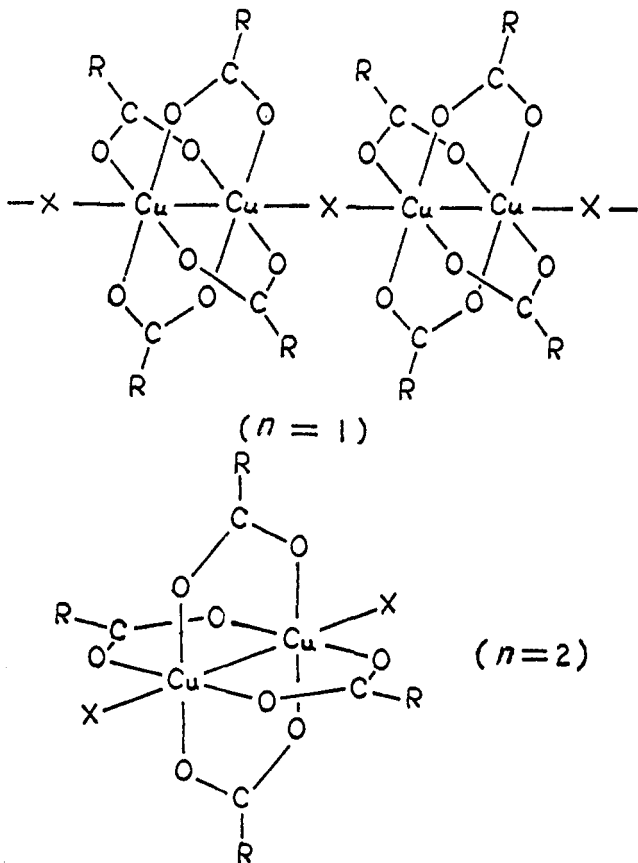
compound II
(1.45 B.M.)
gradually heated or dried over P$_2$O$_5$ at room temperature
→ green powder
(1.44 B.M.)

compound I
(1.92 B.M.)
heated very slowly to 85°
→ blue-green compound
(1.41 B.M.)

heated rapidly at 85° or dried over P$_2$O$_5$ at room temperature
→ brown compound, very hygroscopic
(1.37 B.M.)

Inoue (80, 81) has also prepared some anhydrous modifications of copper(II) benzoate in the following way.

pale greenish blue
(1.7₂ B.M.)

Cu(C₆H₅CO₂)₂·3H₂O

bluish green
(1.40 B.M.)

Cu(C₆H₅CO₂)₂·C₂H₅OH

bluish green
(1.49 B.M.)

It has been verified by X-ray powder diagrams that the structures of the anhydrous compounds with magnetic moments of 1.40 and 1.49 B.M. are different from each other. The compound of 1.49 B.M. may be the same as that for which a magnetic moment of 1.5 B.M. was reported by Ploquin (158).

G. ADDITION COMPOUNDS

The terminal position, marked Y in Fig. 6, of the dimeric copper(II) alkanoates can be replaced with another ligand molecule of moderate coordinating power without breaking the dimeric structure. Many


such addition compounds have been isolated with the general formula $Cu_2(RCOO)_4 \cdot X_n$ ($n = 1$ or 2). The structure shown above might be postulated (79, 136).

It is significant that the magnetic moments of addition compounds of copper(II) acetate or its higher homologs are not very different from those of the parent compounds. The moments of many addition compounds of copper(II) formate are much lower (1–1.1 B.M.) than those of the parent compounds (1.6 B.M.) or than the copper(II) n-alkanoates (1.4 B.M.) (136) (cf. Tables I and III).

V. COPPER(II) COMPOUNDS WITH SUPER-EXCHANGE INTERACTION

A. MAGNETIC PROPERTIES

The copper(II) compounds belonging to this category have a larger copper–copper distance than those with direct copper-to-copper interaction. The space between neighboring copper(II) ions is occupied by one or more diamagnetic atoms. The simplest case may be represented by CuO with a subnormal magnetic moment of 0.78 B.M. (155). Its structure is shown schematically below (175, 188a).
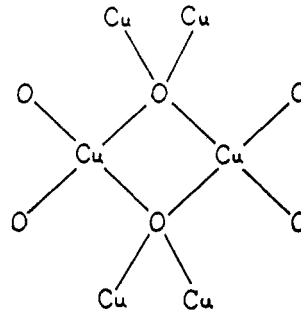
The magnetic interaction of many chelate compounds falls into this category.

1. The So-Called "Tri-Coordinated" Copper(II) Complexes

In 1937, Pfeiffer (157) prepared salicylal-o-hydroxy-anilcopper(II) and, in 1946, Calvin (33) recorded a subnormal magnetic moment of 1.58 B.M. for this compound. However, this anomalous moment was attributed to possible impurities.

Recently Yamaguchi (196) and Muto (143, 144) have synthesized salicylal-o-hydroxybenzylaminecopper-(II). Kishita (104–107, 119, 145) has measured their magnetic susceptibility as well as that of many other new compounds. Most of theses o-called "tri–coordinated" complexes have been found to have subnormal magnetic moments. All monopyridine derivatives of these complexes, however, have normal magnetic moments. In view of the observed subnormal magnetic moments, Kishita (104–107) predicted the existence of binuclear complex molecules for these complexes with a copper–copper distance small enough to permit
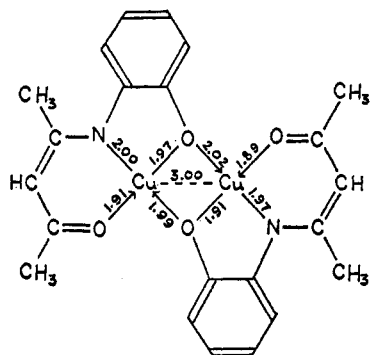
Fig. 10.—Structure of acetylacetone-mono(o-hydroxyanil)-copper(II). The numerical values in the figure are the atomic distances (Å.).

exchange interaction between two copper(II) ions. This prediction has recently been confirmed by the X-ray analysis of acetylacetone-mono(o-hydroxyanil)-copper(II) carried out by Barclay, et al. (10), which is schematically shown in Fig. 10. They obtained the single crystals for X-ray analysis from bromobenzene. It was also found that the magnetic susceptibilities measured over a wide range of temperatures fit Bleaney and Bowers' Eq. 1, used for copper(II) acetate monohydrate. Therefore, Barclay has reported this as the first copper(II) complex which behaves magnetically like copper(II) acetate but does not possess a copper(II) acetate structure (8b,d). The copper–copper distance in copper(II) acetate monohydrate (178, 179) is 2.64 Å. shorter than that in acetylacetone-mono(o-hydroxy-anil)copper(II) (3.00 Å.). However, the J-value in the latter (298 cm.$^{-1}$) is larger than in the former (284 cm.$^{-1}$). This may indicate that in the latter compound the magnetic interaction occurs by way of super-exchange through the bridged oxygen atom rather than by direct copper-to-copper interaction.

In order to elucidate the structure of some tri-co-ordinated complexes with normal moment, Kubo (101, 119) measured the infrared absorption spectra of these compounds. They show the antisymmetric COO^{-} stretching vibrations of the salt-type structure in the range 1583–1599 cm.$^{-1}$, different from those of carbonyl bands of the corresponding free acids, 1633–1705 cm.$^{-1}$.
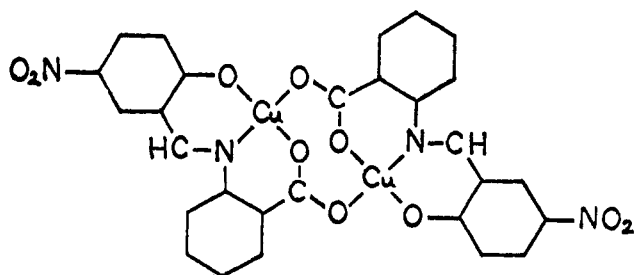

Fig. 11.—Proposed binuclear structure of (5-nitrosalicylanthra-nilic acid)copper(II).

He suggested a new binuclear structure shown in Fig. 11, represented by (5-nitrosalicylanthranilic acid)-copper(II) in which direct spin–spin interaction or super-exchange type interaction are negligible between the two copper(II) ions. He postulated that "tri-coordinated" copper(II) complexes do not exist regardless of whether the complex shows normal or subnormal magnetic moments.

The recent cryoscopic determination of the molecular weights for tri-coordinated copper(II) complexes made by Ohta (153) has shown that N-salicylidene-N'-n-caprinylhydrazinocopper(II) and N-salicylidene-N'-n-palmitylhydrazinocopper(II) are indeed dimeric.

2. Halogen-Bridged Complexes

The copper(II) compounds containing a halogen-bridged structure may have normal or subnormal moments. Recently, the dimeric structure of LiCuCl$_3$·2H$_2$O (182), KCuCl$_3$, and NH$_4$CuCl$_3$ (189)
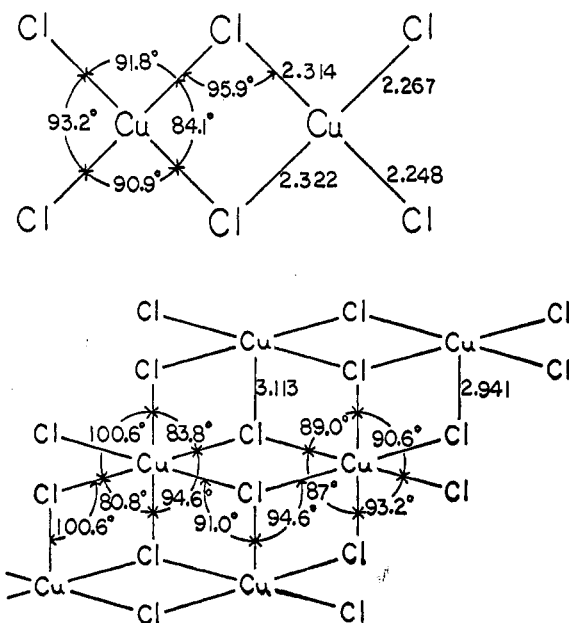

Fig. 12.—The schematic expression of the structure of KCuCl$_3$.

has been confirmed by X-ray analysis. The structure of KCuCl$_3$ in Fig. 12 is representative. The para-magnetism of LiCuCl$_3$·2H$_2$O was examined from room temperature down to 5.9°K., indicating that the ground state is triplet rather than singlet. It was suggested that the ferromagnetism of this compound should be due to the structure with the symmetrically bridged halides. Therefore, the antiferromagnetism of anhy-drous CuCl$_2$, which contains an infinite planar chlorine-bridged chain, must come from interactions between chains rather than super-exchange via chloride bridges (167, 187). KCuCl$_3$ has a maximum susceptibility at about 30°K., probably indicative of antiferromag-netism. However, it appears that, at least at room

temperature, the dimer structure of KCuCl$_3$ and NH$_4$CuCl$_3$ does not lead to diamagnetism. The magnetic moment of KCuCl$_3$ is 1.77 B.M. at room temperature (35). Both compounds are pleochroic with maximum visible absorption when the electric vector is parallel with the copper–copper direction of the dimer.[1] There are many other examples of halogen-bridged copper(II) compounds with normal magnetic moment such as: CsCuCl$_3$, 1.89~1.95 B.M. (35, 43, 186); CuCl$_2$·2H$_2$O, 1.87 B.M. (68, 176, 188b); CuF$_2$· 2H$_2$O, 1.94 B.M. (53, 152); CuCl$_2$·pyridine, 1.8 B.M. (39, 100). However, some of them contain fairly large intramolecular distances.

In most cases, copper(II) complexes containing the bromide ion have moments lower than those of the corresponding chloride complexes. A typical example is anhydrous copper(II) chloride and bromide. They are isostructural (75, 187, 188c), and the magnetic moment of CuCl$_2$ is 1.75 B.M. (108) but 1.31 B.M. for CuBr$_2$ (155).

Fluoride complexes also may have normal or subnormal magnetic moments. KCuF$_3$, μ = 1.38 B.M., is a typical example of this type (130, 133). The perovskite structure is considered to be particularly suitable for super-exchange since it contains an infinite, linear, three-dimensional M–F–M–F array (40). The moment of CuF$_2$ is 1.4–1.5 B.M. (38, 76), but CuF$_2$·2H$_2$O has a slightly high moment of 1.94 B.M. (152). One of the reasons for such difference in magnetic behavior seems to be due to the different distances between a copper(II) ion and a fluoride ion attached to the nearest neighboring metal ion. The distance of Cu–F···Cu is 2.27 Å. in CuF$_2$ (22, 188d) but 2.47 Å. in CuF$_2$·2H$_2$O (53).

3. Copper(II) Complexes with N-Oxides and Some Related Compounds

Quagliano (161) has prepared (pyridine N-oxide)-copper(II) complexes, Cu(PyO)Cl$_2$, and Cu(PyO)$_2$Cl$_2$ (PyO = C$_5$H$_5$NO) having abnormally low magnetic moments; however, he did not attempt to explain this phenomenon. Harris (71) has prepared Cu(PyO)Cl$_2$, Cu(PyO)Br$_2$, and the corresponding (quinoline N-oxide)copper(II) complexes. The anomalously low magnetic moments were confirmed for these compounds and indicate the existence of a very large magnetic interaction. This is confirmed by the study of the temperature variation of magnetic susceptibilities for Cu(PyO)Cl$_2$. The measured J-value of 2 kcal. is quite large. Kishita (103) has also prepared the same compounds as well as the addition compounds with dimethylformamide and dimethyl sulfoxide. Similar

(1) Note Added in Proof.—Very recently Willett and Rundle (*J. Chem. Phys.*, **39**, Feb., 1964) have determined the crystal structures of the three red complexes, Cu$_2$Cl$_4$(CH$_3$CN)$_2$, Cu$_2$Cl$_6$(CH$_3$CN)$_2$, and Cu$_3$Cl$_{10}$(C$_3$H$_7$-OH)$_2$. All these complexes contain the same type of a chlorine-bridged structure. The same type of pleochroism was also confirmed with these complexes. The correlation of the deep red or yellow coloration with the symmetrical Cu–Cl–Cu bridge with short bonds (~2.3 Å.) was established.
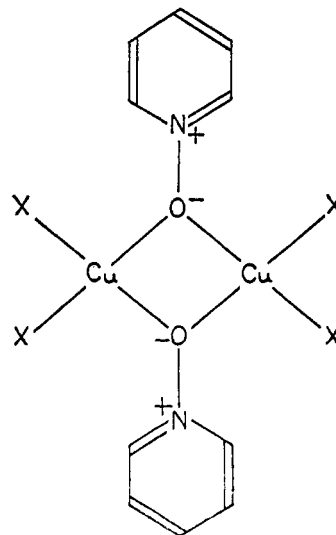

Fig. 13.—The suggested structure of pyridine N-oxide Cu(II) complexes; X = Cl or Br.

magnetic features were observed for these compounds. The binuclear oxygen-bridged structure shown in Fig. 13 was suggested for these compounds (71, 103, 119) based on the structure of acetylacetone-mono(o-hydroxyanil)copper(II). The super-exchange interaction can occur between the pair of copper(II) ions in the molecule via the oxygen atoms. Two dimeric structures can exist which could be responsible for the antiferromagnetism, an oxygen-bridged (Fig. 13) and a halogen-bridged one (Fig. 14). The oxygen-bridged structure seems to be more probable. The negatively charged oxygen atom will produce a more stable bond to the copper(II) ion than the halide ion. The pK values of CuCl$^+$ and CuBr$^+$ are fairly small, 0.11 and 0.30, respectively, whereas the pK value of CuOH$^+$ is very large, 6.47 (197). Furthermore, the copper(II) ions in the oxygen-bridged structure are surrounded by two oxygens and two halogens; in the halogen-bridged structure, on the other hand, they are surrounded by one oxygen and three halogens. However (57), the structure of [Cu(Ph$_3$AsO)$_2$Br$_2$] has been considered to be dimeric from its subnormal magnetic
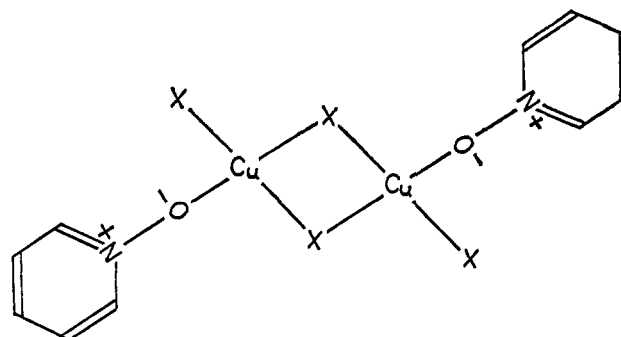

Fig. 14.—Halogen-bridged structure of pyridine N-oxide Cu(II) complexes; X = Cl or Br.

moment of 1.56 B.M., whereas [Cu(Ph₃PO)₂Br₂], judging from its slightly high moment of 2.01 B.M., seems not to be dimeric. The main difference between the two compounds lies in the arsenic and phosphorus. The oxygen atom bound to the less electronegative arsenic combines with the copper(II) ion tightly enough to keep the dimeric structure. Recent observations by Muto and Jonassen (146) also indicate that the strong Cu–O bond is necessary to maintain a dimeric structure. Pyridine N-oxide (pK of H⁺L, 0.79) (87) combines with cupric chloride or bromide to produce complexes with subnormal magnetic moments from alcoholic solution; however, 4-nitropyridine N-oxide, with a pK value of −1.7, does not form complexes in the same solvent (87).

Halogen-bridged structures will produce the paramagnetic complexes, especially in the chlorides (cf. section VA2).

Very recently, copper(II) complexes of quinoline N-oxide and 4-methylpyridine N-oxides with very low magnetic moments have been prepared by Harris (71) and Muto (146). A good correlation between the pK values of the N-oxides and the magnetic interaction in the complexes is observed (cf. section VC).

Fanning and Jonassen (41, 42) have recently prepared copper(II) compounds of 8-hydroxyquinoline(hqn) having the empirical formula Cu(hqn)X (X = Cl or Br) by dissolving equivalent amounts of copper(II) halide and hqn in absolute methanol or acetone. Subnormal magnetic moments of 0.87 and 1.10 B.M. were determined for chloride and bromide compounds. Harris, et al. (70), have prepared the Cu(hqn)Cl by a different method, treating copper(II) chloride with Cu(hqn)₂ in boiling ethanol. They also prepared Cu(hqn)(NO₃)·H₂O and [Cu₂(hqn)₃]ClO₄·0.5C₂H₅OH. All of these compounds have subnormal magnetic moments of 1.14, 1.39, and 1.60 B.M. for the chloride, nitrate, and perchlorate. They suggested a binuclear oxygen-bridged structure for these complexes (Fig. 15). The μ–T or χ_M–T curves for Cu(hqn)(NO₃)·H₂O were in agreement with those calculated from Bleaney and Bowers' Eq. 1, supporting its

dimeric structure. On the other hand, they suggested a polymeric structure for Cu(hqn)Cl because the susceptibility curve did not fit that calculated. It was, however, pointed out that an admixture of a small amount of the halogen-bridged isomer in the paramagnetic state with the compound in the antiferromagnetic state could lead to the observed deviation of the χ_M–T curve from the theoretical one based on Eq. 1 (90).

4. OH-Bridged Complexes

Hatfield (74) has measured the temperature variation of magnetic susceptibilities for Cu(amine)(OH)(ClO₄), [amine = (C₂H₅)₂NCH₂CH₂NHCH₃ (I) or (C₂H₅)₂-NCH₂CH₂N(C₂H₅)₂ (II)]. The magnetic moments at room temperature are 1.69 and 1.38 B.M. for I and II. The observed antiferromagnetic character of these compounds strongly supports Pfeiffer and Glaser's formulation as binuclear complexes with hydroxy bridges (156). The steric requirements of the N-alkyl groups are postulated to promote the formation of such binuclear complexes (13, 14, 131). He calculated the mole fractions of molecules in singlet and triplet states from the magnetic moments by assuming the singlet state to have a moment of 0.0 B.M. and the triplet state a moment of 2.90 B.M. Based on the mole fractions, equilibrium constants for the reaction, singlet ⇌ triplet, were calculated at various temperatures. From the set of equilibrium constants, ΔH° and ΔS° of the reaction were calculated by ordinary thermodynamic methods. The ΔH° values of 1.06 and 1.49 kcal./mole for I and II obtained in this manner are in good agreement with the J-values of 1.07 and 1.17 kcal./mole calculated based on Eq. 1. The observed entropy change of 2.2 to 2.6 e.u. is also in good agreement with the value of 2.2 e.u. calculated from R ln 3 where 3 is the degeneracy ratio of the triplet and singlet states, assuming that the only contribution is that from the electronic entropy.

Bergeret and Jonassen (17) have prepared copper(II) compounds of o- and p-toluic acid, having the formula Cu(II) o-toluate·OH·0.5o-toluic acid (I) andCu(II) p-toluate·OH·0.5p-toluic acid (II) by treating CuSO₄·5H₂O and o- or p-toluic acid in a 50–50 mixture of methanol and water neutralized to pH 3.5 with OH⁻ ions. In line with Pfeiffer's (156) and Hatfield's (74) results, the observed magnetic moments of 1.72 and 1.82 B.M. for I and II are indicative of the OH-bridged binuclear structures in these compounds. Thieleman and Jonassen (168) have observed a break on a magnetometric titration curve of a solution containing equimolar quantities of copper(II) chloride and 2,2′,2″-triaminotriethylamine (tren)·3HCl with sodium hydroxide at the point where 4 equivalents of alkali is added. Cu·tren·OH⁺ is considered to be present in solution as the dimeric species
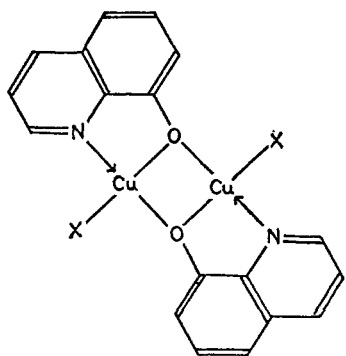

Fig. 15.—The proposed binuclear structure of copper(II) compounds with 8-hydroxyquinoline and X; X = Cl, Br, or NO₃.
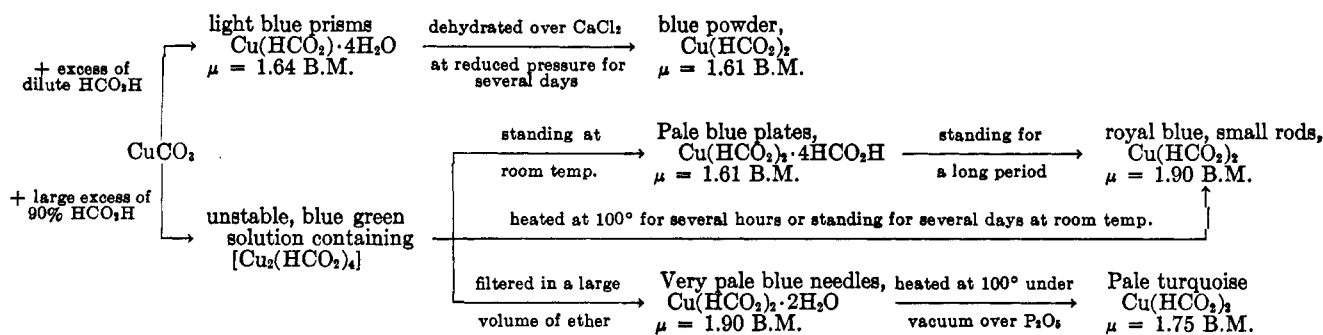
Fig. 16.—Diagram of the preparation method of the modifications of copper(II) formate.

$$\left[Cu \begin{array}{c} OH \\ \diagdown \\ \diagup \\ OH \end{array} Cu \right]^{+2}$$
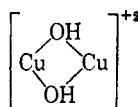
and super-exchange through the bridging OH⁻ ions leads to the lowering of the magnetic moment (cf. also ref. 142).

5. Copper(II) Complexes with More than One Bridging Atom

a. Copper(II) Formate

The magnetic interaction of the compounds which have more than one intervening atom between the copper(II) ions is also of great interest. The X-ray structural analysis of copper(II) formate tetrahydrate was made by Kiriyama (cf. Fig. 5) (98). Martin (135) discussed the subnormal magnetic moment of 1.64 B.M. in terms of super-exchange interaction between copper(II) ions via the formate group (cf. section VC).

As mentioned in section I, copper(II) formate appears in a variety of modifications. The preparation methods of several copper(II) formates are shown diagrammatically in Fig. 16 together with the magnetic data (135). These modifications were characterized by X-ray diffraction. Copper(II) formate–tetraformic acid and the anhydrous blue compounds have a magnetic moment of 1.61 B.M. They seem to have the same type of magnetic interaction as the tetrahydrate.

Recently, the royal blue form of anhydrous copper(II) formate, $\mu = 1.90$ B.M., has been examined by X-ray analysis (11). The elucidated structure (Fig. 17) would be expected to lead to an antiferromagnetic interaction between copper(II) ions similar to that in the tetrahydrate. The important difference between the tetrahydrate and the anhydrous compounds lies in the coordination above and below the square-planar complex around each copper(II) ion. The tetrahydrate completes a distorted octahedral coordination to combine with two water molecules in the trans position of the complex containing the formate ion. In the anhydrous compound, however, each copper(II) ion completes a distorted tetragonal-pyramidal coordination with four oxygen atoms in a plane containing the copper(II)
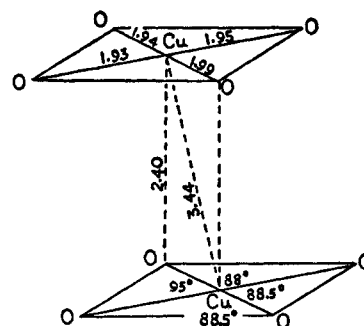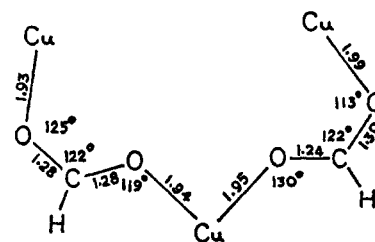
Fig. 17.—Schematic expression of the structure of copper(II) formate, anhydrous, royal blue form, $\mu = 1.90$ B.M.

ion and a fifth oxygen atom from the formate ion attached to a copper(II) ion which is in a neighboring layer; this produces a dimeric structure.

The observed magnetic moment of the anhydrous compound can be explained by an increase of the magnetic moment due to a tetragonal-pyramidal configuration. The magnetic moments of elongated octahedral complexes of copper(II) have been postulated to be larger than the spin-only value, about 1.8–1.9 B.M. (43, 84). This magnetic moment in the tetrahydrate may then be decreased to 1.6 B.M. by super-exchange. Boudreaux (30) calculated the magnetic moment of square-pyramidal copper(II) complexes to be 2.1–2.2 B.M. at room temperature. The original value of about 2.1–2.2 B.M. for the square-pyramidal anhydrous compound may be decreased to the observed value of 1.9 B.M. through super-exchange similar to that observed for the distorted octahedral.

Similar observations have been reported for the following series of compounds (33).

$n = 2, 5, 6, - - -$
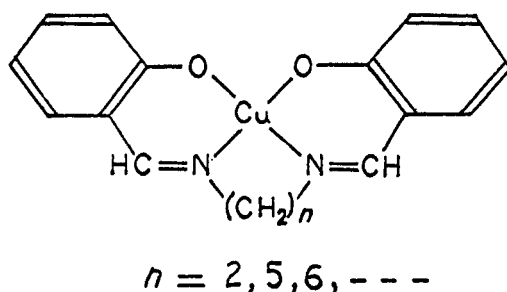
A magnetic moment of 1.86 B.M. was observed for bis(salicylaldehyde)copper(II) whose structure has recently been found by X-ray analysis to be square-planar (18). Aromatic carbon atoms at a long distance, 3.24 Å. above and below the molecular plane, are the nearest neighbors to the copper(II) ion. The square-planar nature of the complex is supported by the ob-servation that the visible region solid-state reflectance spectrum of this compound is virtually the same as the solution spectra in chloroform (18). N,N'-Disalicyli-deneethylenediaminecopper(II) $(n = 2)$, which has a dimeric structure completing a square-pyramidal com-plex (cf. Fig. 18) (65), shows a fairly large magnetic

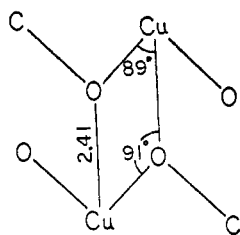

Fig. 18.—Dimeric configuration of N,N'-disalicylideneethylene-diaminecopper(II).

moment of 2.04 B.M. (33); however, the moment decreases to 1.83–1.84 B.M. for the compounds of n = 5 and 6.

N,N'-Disalicylidenepropane-1,2-diaminecopper(II) monohydrate exhibits a square-pyramidal config-uration with a water molecule at the top of the pyra-mid (Fig. 19) (128). Its magnetic moment is 1.86 B.M. at 298°K.; this decreases to 1.71 B.M. at 298°K. when dehydrated (66).

The high moment of the royal blue form of anhy-drous copper(II) formate may also be produced due to ferromagnetic spin interaction of the copper(II) ions
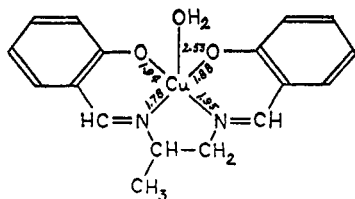

Fig. 19.—Schematic expression of the structure of N,N'-disalicyl-idenepropane-1,2-diaminecopper(II) monohydrate.

between layers. This could lead to the observed high moment of 1.9 B.M., increased from the original value of 1.6 B.M., the value for the tetrahydrate (cf. section VC).

One of the possible explanations for the lowering of the magnetic moments of copper(II) alkanoates on removal of the terminal water molecule might be found in a similar mechanism. Removal of the water mole-cule attached to the copper(II) ion will make the square-pyramidal coordination less effective, leading to the slight lowering of the magnetic moment (cf. Fig. 1).

b. Copper(II) Benzoate

Recently the X-ray structural analysis of copper(II) benzoate trihydrate has been completed by Koizumi (111, 112). The structure is shown schematically in Fig. 20. It is of great help in the correlation between
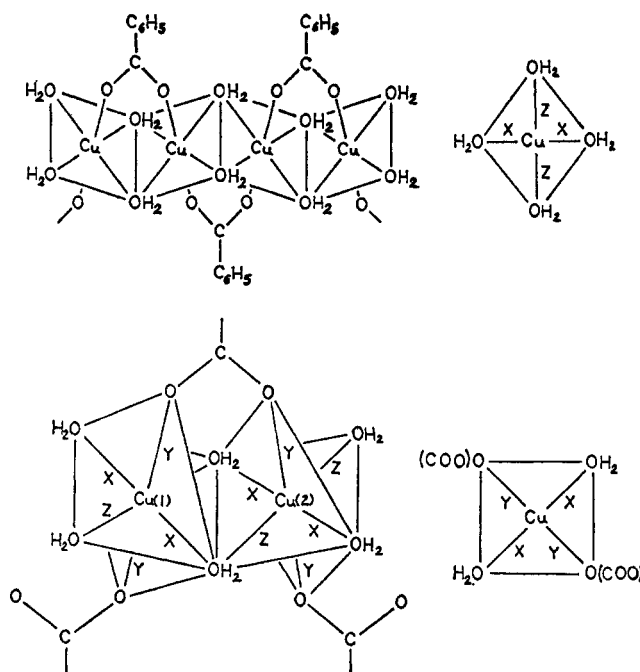
Fig. 20.—Schematic expression of the structure of copper(II) benzoate trihydrate: $x = 1.97$, $y = 1.91$, $z = 2.51$ Å., Cu–Cu = 3.15 Å.; $(xy)_1$–$(xy)_2$ angle = 56°30' or 123°30'; $(xz)_1$–$(xz)_2$ angle = 31°14' or 148°46'; (COO)–$(xy)_1$ angle = 77°13' or 102°47'; (COO)–$(xy)_2$ angle = 59°15' or 120°45'.

the degree of magnetic interaction and the bond lengths or orbital overlaps. Inoue (80, 81) has prepared the compound in the same way as that used for the prepara-tion of the sample for X-ray analysis and measured its magnetic susceptibility; he obtained a magnetic mo-ment of 1.87 B.M. This is not surprising since the copper–copper distance of 3.15 Å. is much larger than that in copper(II) acetate monohydrate (2.64 Å.) (178, 179), and since the orientation of the 3d orbitals of the copper(II) ions is not suitable to produce effec-tive overlap for direct copper-to-copper interaction.

On top of this, orbital overlaps of a π-pathway for super-exchange are also insufficient (cf. sections III and VC).

The crystal structure of $CuCl_2(1,2,4\text{-triazole})$ is very similar to that of copper(II) benzoate trihydrate (88). Two nitrogen atoms of the triazole molecule replace the two oxygen atoms of the carboxylate group. Chloride ion bridges are formed instead of H_2O bridges. The magnetic moment of this compound is 1.81 B.M., as expected from its structure (82). It is interesting to note, however, that copper(II) sulfate combines with triazole to produce $CuSO_4(1,2,4\text{-triazole})\cdot 4H_2O$ with a subnormal magnetic moment of 1.62 B.M., different from that of copper(II) chloride·triazole (82). Two modifications for bis(triazolato)copper(II), $Cu(C_2H_2N_3)_2$, have been prepared, the magnetic moments of which are 1.4 and 1.66 B.M. (82).

c. Copper(II) Compounds with Substituted Benzoquinone

Recently, Kobayashi (73, 110) has measured the magnetic susceptibilities of 2,5-dihydroxy-p-benzoquinonecopper(II) (I), chloroanilinecopper(II) (II), and bromoanilinecopper(II) (III) at low temperatures.

X = H (I), Cl (II), Br (III)
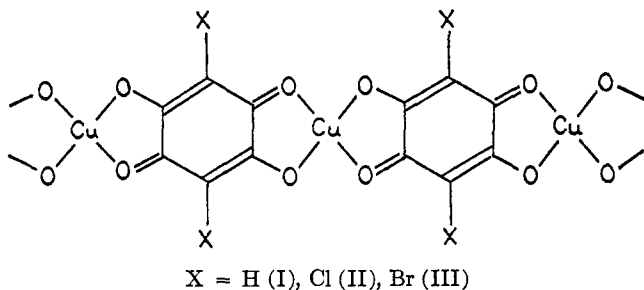
A super-exchange interaction of $J = 10\text{--}17$ cm.$^{-1}$ was obtained for compound I. The exchange interaction is not very much influenced by changing the H atom on I by a Cl or Br atom.

Magnetic susceptibilities of one-dimensional lattices containing spin values of 2 to 10 were calculated by Griffiths (63). The result indicates that the temperature dependent magnetic behavior of this type of compound depends upon whether the compounds contain an odd or even number of electrons. Griffiths' results indicate that compound I seems to have an odd number of electrons greater than 9.

B. SPECTRAL PROPERTIES

1. Visible and Ultraviolet Regions

The band at 375 mμ of copper(II) alkanoates was discovered by Tsuchida (169, 193) and assigned to the band indicative of the presence of a direct copper-copper bond. This band assignment was partly based on the known structure of copper(II) acetate monohydrate. This band is at present the reason for considerable controversy (section IVD). No systematic study of the absorption spectra in the visible and ultraviolet regions has appeared for the copper(II) compound with magnetic interaction of the super-exchange type. Some descriptions of absorption bands are, however, found in a few papers (41, 42, 57).

2. Infrared Spectra

Quagliano (93, 96, 161) has determined the infrared spectra of many metal complexes containing pyridine N-oxide and has made assignments for many bands. However, it is still rather difficult to correlate the observed bands in these copper(II) compounds with their magnetic behavior.

C. FACTORS CONTROLLING SUPER-EXCHANGE INTERACTION

(Contributed by L. C. Cusachs, M. Kato, and H. B. Jonassen)

Martin and co-workers (135) discussed the mechanism of the super-exchange interaction responsible for the small lowering of the magnetic susceptibility of cupric formate tetrahydrate; their paper made use of the theory at an intermediate stage of development. Recent contributions by Anderson (5), by Goodenough (56), and by Nesbet (148) give a somewhat simpler and clearer theoretical account. Some extension is necessary to adapt the model to transmission by polyatomic groups such as formate ion, where there are several orbitals of both relevant symmetry classes, so that it is not so easy to single out one orbital as the primary link, coupling the spins in the copper sublattices.

Super-exchange should be regarded as incipient covalent bonding. Nesbet (150) goes so far as to interpret the bonding in inert gas halides, e.g., XeF_2, as cases of very strong super-exchange, where the halogen-bonding electrons are coupled through a filled inert gas p orbital. This model is formally equivalent to the simplest molecular orbital picture involving only orbitals occupied in the free atoms. Anderson (4, 5) points out that the metal molecular orbitals will not be the simple symmetry orbitals (this symmetry being irrelevant in the sense of Jørgensen (91b)), but rather localized Wannier functions or the alternate molecular orbitals of Löwdin (129), "different orbitals for different spins." This is because the double occupancy of symmetry orbitals leads to electron repulsion of both one and two center types. The latter become very small at nonneighbor distances, but the former remain large, effectively localizing the electrons on separate atoms. In ordinary molecular-orbital language, this would be described by configuration interaction with a double excited singlet canceling out the one-center repulsion terms, but still requiring the electron-spin pairing for interaction with the carrier group.
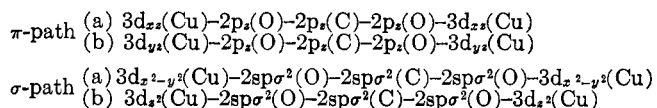
Goodenough (56) obtained a set of simple rules from

plausible postulates permitting him to rationalize the extensive magnetic data on first-transition series oxides and halides. Nesbet (148) supplied an elegant theoretical foundation for the postulates by direct calculations on the nitrogen molecule over a range of internuclear distances. His calculations revealed three interesting molecular ranges of nuclear separation in which different electron-spin coupling arrangements constituted unique, best, first approximations to the electronic-wave function. For N_2, the 1s and 2s atomic orbitals and the molecular orbitals, which they correlate, are completely filled, so that the 2p atomic and related molecular orbitals are the only ones for which more than one distinct possibility exists for the lowest configuration. In the first region, from inside the equilibrium internuclear distance to roughly one and one-half times that distance, a description in terms of doubly-occupied molecular orbitals is appropriate for both p-σ and π electrons. In a second region, the p-σ coupling is still strong enough to pair up the electrons (antiferromagnetic), while the π electrons are coupled parallel (ferromagnetic) in the best one-term description. A third region was found where all p electrons were coupled parallel. Spins would be random or uncoupled at even greater distances. This result substantiates Goodenough's assumption that interactions involving subclasses of p or d shells may be sufficiently different that a model treating the subclasses differently, i.e., localized or collected into bands or bonds, may be called for. The possibility of super-exchange requires not only that overlap between coupled metal orbitals and the carrier orbital(s) be permitted by symmetry, but also that they occupy a certain amount of common space.

For the copper(II) formate tetrahydrate structure, there is effectively only a plane of symmetry permitting a classification of orbitals as σ and π. From the X-ray results alone, it is possible to confirm the presence of super-exchange because the copper ions are not quite in the center of the distorted oxygen squares formed by formate ions connecting pairs of them. Jahn–Teller distortion would leave the metal ions in the center of a ligand arrangement of reduced local symmetry, while super-exchange is expected to displace the ions toward the formation of magnetically-paired sublattices (Goodenough). Low-temperature magnetic data (46, 109) require at least this degree of complexity.

Martin (135) considered three factors as primary in finding the path of lowest energy for migration of the unpaired 3d electron associated with magnetic interaction: (a) the relative energies of alternate paths, (b) the "transmission probability" associated with each path, which will be at least roughly proportional to the orbital overlap between copper and formate oxygen atoms, and (c) the relative energies of the ground

and excited states of copper under the influence of the ligand. For migration of an electron, the formate ion provides two paths of different symmetry, σ or π, as follows.

π-path (a) $3d_{xz}(Cu)-2p_z(O)-2p_z(C)-2p_z(O)-3d_{xz}(Cu)$
(b) $3d_{yz}(Cu)-2p_z(O)-2p_z(C)-2p_z(O)-3d_{yz}(Cu)$

σ-path (a) $3d_{x^2-y^2}(Cu)-2sp\sigma^2(O)-2sp\sigma^2(C)-2sp\sigma^2(O)-3d_{x^2-y^2}(Cu)$
(b) $3d_{z^2}(Cu)-2sp\sigma^2(O)-2sp\sigma^2(C)-2sp\sigma^2(O)-3d_{z^2}(Cu)$

Overlap between the $3d_{xy}$ (and $3d_{z^2-y^2}$) orbital of copper and the oxygen p-π orbitals is excluded by symmetry in the structure elucidated by X-ray. Utilization of the σ-path is assumed to be associated with a gross-energy barrier, though the presence of a number of σ-orbitals in the formate ion calls for a calculation to find out whether a suitable single orbital or a collective mechanism is substantiated. No such restriction would apply to the π-path involving delocalized electrons though this mechanism requires starting from the less favorable d_{xz} or d_{yz} orbitals and π-overlap is usually less than σ-overlap for the same orbitals differently oriented. Martin suggested that a $3d_{xz}$ or $3d_{yz}$ electron should be promoted to the $3d_{z^2-y^2}$ orbital so that a π-path can be available. According to Polder's calculation (160) or the result obtained experimentally by Graddon (62) for copper(II) alkanoates, energy of about $21,000\sim27,000$ cm.$^{-1}$ is required to accomplish this. The choice of a σ- vs. a π-pathway for the super-exchange depends then on whether the promotional energy involved in the $3d_{xz}$ or $3d_{yz}$ → $3d_{z^2-y^2}$ transition for copper is greater or less than the energy barrier relative to the mobility of an electron of the highly localized σ-bonding orbitals of the OCO framework.

They preferred the π-path to the σ-path based on the consideration that "preconditioning" copper, for which energy of about $21,000\sim27,000$ cm.$^{-1}$ is necessary, will be energetically easier than "preconditioning" the σ-pathway, although the energy barrier for the latter process is difficult to estimate. However, the final energy balance in terms of the excited and ground states (4, 115) is independent of which 3d orbital has been used for the super-exchange interaction. In this sense, the π-pathway will be more favorable than was supposed by Martin for cupric formate tetrahydrate.

Reviewing the discussion of Martin based on early work by Kramers (115) and the first Anderson paper (4), the primary factors to evaluate are the bond or transmission integral between the metal and ligand orbitals, roughly proportional to the overlap, the metal excitation energy, arising from the energy-level difference between orbitals (crystal-field stabilization energy), and the relative energy of the ligand and metal orbitals. The last two terms, related to Coulomb parameters (orbital-ionization energies), are not involved in the direct copper-to-copper interaction, e.g.,

copper acetate (compounds under classification A, *cf.* IIIA).

From the more recent Anderson–Goodenough–Nesbet viewpoint (4, 5, 56, 149), that of incipient covalent bonding, we have the general condition that the interacting orbitals (Coulomb parameters) are not too different. Electron-repulsion parameters would be of secondary importance in determining the localization of the coupled metal electrons. The super-exchange energetics can be arbitrarily divided into the stabilization of the carrier orbital(s) and the shift of the metal levels. Assuming a single ligand carrier, as in the oxides and halides, taken as more electronegative than the metal, the stabilization of the ligand is

$$\Delta E = \frac{2S^2 E_m}{E_m - E_1}$$

per electron, while the metal pair is destabilized by the amount

$$\Delta E = \frac{-S^2 E_1}{E_m - E_1}$$

per electron, assuming nearly complete localization (configuration interaction), where S is the metal–ligand overlap, E_m is the metal Coulomb parameter, and E_1 the ligand parameter. This perturbation treatment assumes the Wolfsberg–Helmholz approximation under conditions of doubtful validity (36). It would be somewhat more difficult to extend this to include the effect that each formate ion interacts with only two cupric ions, while each of the latter is in contact with four formates, each of which has 10 principal σ-orbitals, seven of which are occupied. The π-system contains three orbitals, two of them occupied. A detailed calculation is called for. The principal two-electron (exchange) term will favor parallel spins but should be much smaller than the one-electron term if this is present at all.

For a single-carrier orbital, it is easy to see that a π-path does not depend on bond angles, requiring only coplanarity, while a p-σ orbital cannot simultaneously overlap metal atoms subtending a right angle at its center; maximum overlap is obtained if the three orbitals are colinear.

Magnetic moments less than solution values are well accounted for by the super-exchange model. Semiquantitative calculations appear to be feasible and should be expected to show whether additional features need be examined. A difficulty arises where the simplest theory may explain too much; for example, the moment (1.90 B.M.) of the anhydrous copper(II) formate (135) is high for a square-planar model with super-exchange. If the environment is accepted to be square-pyramidal (11), there arises an orbital contribution leading to an estimated 2.11 B.M. before super-exchange (30), entirely consistent with the model. On the other hand, a quenched square-

planar copper (85) might have its observed moment appreciably raised by ordinary ferromagnetic (direct) exchange at the observed distance of 3.44 Å., though this is a bit far. Calculations of orbital-contribution variation with distortion for moderate deviations from high symmetry would be helpful here. The first explanation has the great attraction of permitting hope that the effect of the neglected terms (high frequency, etc.) is generally negligible and not just a fortunate cancellation in the present case.

The bond angle, Cu–O–Cu, of acetylacetone-mono(*o*-hydroxyanil)copper(II) determined by X-ray analysis (10) seems to be almost rectangular indicating that the utilization of p-σ bonding for super-exchange interaction is just about impossible. However, the π-pathway with the $3d_{xz}$ or $3d_{yz}$ orbital of copper and p orbital of oxygen and σ-pathway with the $3d_{x^2-y^2}$ or $3d_{z^2}$ orbital of copper and s orbital of oxygen can be set up in this case. Magnetic interaction through a σ-pathway is considered to decrease in strength very fast as the number of intervening atoms between the metals increases. However, this is not the case for the compounds with the acetylacetone-mono(*o*-hydroxyanil)copper(II)-type structure. No such drop in magnetic interaction with the increasing number of intervening atoms is expected in the case of a π-pathway. It is, however, not easy to evaluate the above factors separately.

However, it can be seen in Table IX that some correlation exists between the magnetic moments and the coordinating power of coordinated atoms or the nature of the substituents on the molecule. These physico-chemical properties of the metal and ligands show close correlation with the coulombic integral of atomic orbitals in the metals and in the coordinating atoms of ligands or the overlap integral between them. The difference in magnetic interaction between compounds 1 and 2 in Table IX is due to the difference in the donating power of the coordinated atoms of the

Table IX

	Compound	μ, B.M.
1	Salicylal-2-hydroxybenzylaminecopper(II)	0.87
2	Salicylal-*o*-hydroxyanilcopper(II)	1.34
3	Benzoylacetone-mono(*o*-hydroxyanil)copper(II)	1.11
4	Acetylacetone-mono(*o*-hydroxyanil)copper(II)	1.37
5	Salicylaldehydebenzoylhydrazonecopper(II)	1.08
6	Salicylaldehyde-*p*-hydroxybenzoylhydrazone-copper(II)	1.02
7	(Pyridine N-oxide)copper(II) chloride	0.73
8	(Quinoline N-oxide)copper(II) chloride	0.36
9	(3-Methylpyridine N-oxide)copper(II) chloride	0.55
10	(4-Methylpyridine N-oxide)copper(II) chloride	0.52
11	(2,6-Dimethylpyridine N-oxide)copper(II) chloride	0.22
12	5-Bromosalicylaldehyde-*o*-mercaptoanilcopper(II)	1.76
13	Salicylaldehyde-2-mercaptoanilcopper(II)	1.82
14	2-Hydroxy-5-methylbenzaldehyde-*o*-mercapto-anilcopper(II)	1.93

respective compounds. This can be estimated from the pK values of benzylammonium ion (9.46) and anilinium ion (4.62) (24). Compound 1, with atoms of stronger coordinating power, then involves magnetic interaction larger than that of compound 2, with atoms of weaker coordinating power. The same trend can be seen for compounds 3 and 4 where the magnetic interaction in compound 3 is larger than that in compound 4. The order of the magnitude of the pK values of HL or the stability constants of the copper complexes of benzoylacetone and acetylacetone (24), which can be considered to be the parent compounds of these complexes, is in the same direction as that of the magnetic interaction. The same sort of comparison can be made between compounds 5 and 6, and 7 and 8. The pK values of benzoic acid and *p*-hydroxybenzoic acid, which are the parent compounds of the copper complexes 5 and 6, are 4.18 and 4.54 (158). The lower magnetic moment of compound 6 is consistent with the larger pK value of its parent compound. The pK values (H$^+$L) of pyridine N-oxide and quinoline N-oxide are 0.56 and 0.70 (120), and (quinoline N-oxide)-copper(II) chloride has a magnetic interaction much larger than (pyridine N-oxide)copper(II) chloride. The pK values of pyridine N-oxide, 3-methylpyridine N-oxide, and 4-methylpyridine N-oxide, reported by Jaffé and Doak (87), are 0.79, 1.08, and 1.29, respectively. Again the same correlation can be observed between the magnetic moments of the copper(II) complexes and the pK values of the N-oxides (146). The pK value of 2,6-dimethylpyridine N-oxide should be larger than that of 4-methylpyridine N-oxide. The magnetic moment (0.22 B.M.) for (2,6-dimethyl-pyridine N-oxide)copper(II) chloride seems to be the lowest found at room temperature (146).

The effect of substituting other elements for the oxygen group in the tri-coordinated copper(II) complexes is observed in the three tri-coordinated copper(II) complexes 12–14 in Table IX. These may have a bridging sulfur atom and show normal magnetic moments (145) which decrease in the decreasing order of the inductive effect $CH_3 > H > Br$.

VI. CONCLUSION

On the basis of present investigations, copper(II) compounds with subnormal magnetic moments can be roughly divided into two types.

Those with direct copper-to-copper interaction have short copper–copper distances. In these compounds, of which copper(II) acetate monohydrate is an example, the bonding is postulated to be of the δ-bond type.

In the second group, represented by acetylacetone-mono(*o*-hydroxyanil)copper(II), super-exchange interaction produces the lowering of the magnetic moments.

It is hoped that this review will initiate structural and other investigations of these extremely interesting compounds.

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