it was discovered that the yields of this salt could be slightly increased by using excess $Na_2S_2C_2(CN)_2$ in the initial reaction between the carbonyl halide and the sulfur ligand. These observations prompted an investigation of the reactions between excess $Na_2S_2C_2(CN)_2$ and the carbonyl halides and cyclopentadienyl maleonitrile dithiolato complexes described earlier in this paper.

Treatment of $(\pi\text{-}C_5H_5)_2TiCl_2$, $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$, $[\pi\text{-}C_5H_5TiS_4C_4(CN)_4]^-$, and $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with excess $Na_2S_2C_2(CN)_2$ almost certainly resulted in the cleavage of the $\pi\text{-}C_5H_5$ ring. It is thought that unsubstituted maleonitrile dithiolato complexes were formed since red-brown solids which were precipitated on addition of heavy organic cations exhibited infrared spectral features similar to known simple maleonitrile dithiolato compounds.[20] However, these solids defied purification, and hence characterization, although on one occasion a low yield of $[(C_6H_5)_4As]_2[FeS_6C_6(CN)_6]^7$ was isolated. $[(C_6H_5)_4P]_3[CoS_6C_6(CN)_6]$ was obtained from $\pi\text{-}C_5H_5CoS_2C_2(CN)_2$, and nickelocene afforded a moderate yield of $[(C_6H_5)_4P]_2[NiS_4C_4(CN)_4]$. Only $\pi\text{-}C_5H_5W(CO)_3Cl$ and $[\pi\text{-}C_5H_5WS_4C_4(CN)_4]^-$ were inert to further attack by $Na_2S_2C_2(CN)_2$ even after refluxing together for several hours in methanol. Behavior of this kind was not observed with bis(perfluoromethyl)dithiete, although derivatives of the type $MS_6C_6(CF_3)_6$, M = Fe, Cr, Mo, or W, were obtained by allowing the appropriate carbonyls and $S_2C_2(CF_3)_2$ to react.[3b]

Acknowledgment.—We wish to thank the Enjay Chemical Co. for a gift of dicyclopentadiene and the International Nickel Co. (Mond) Ltd. and Badische Anilin Soda-Fabrik A. G. for gifts of iron pentacarbonyl and molybdenum hexacarbonyl, respectively.

[20] E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

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Spin-Spin Coupling in Binuclear Complexes. II.
The Magnetic Properties of Schiff's Base Complexes of Copper(II)[1]

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The magnetic behavior as a function of temperature has been determined for a number of binuclear copper(II) complexes with Schiff's bases derived from the condensation of substituted and unsubstituted salicylaldehydes with substituted and unsubstituted *o*-aminophenols. The magnetic properties are markedly affected by the nature and the position of the substituent on the chelate ring. Only one compound exhibited simple copper acetate like behavior. The data for the other compounds indicated that the systems were complicated by the presence of isomers and by inter- as well as intramolecular interactions. The spectra of selected compounds were studied as a function of temperature. There was no significant effect on either band position or intensity.

Introduction

Because of their low magnetic moments the copper complexes with tridentate Schiff's bases formed by the condensation of *o*-aminophenol with salicylaldehyde or acetylacetone have attracted much attention since they were initially reported by Kishita, Muto, and Kubo.[2] The Japanese workers attributed the low magnetic moments of these compounds to either tricoordination of the copper(II) ion or to dimerization in the solid state leading to a direct copper–copper interaction. In 1961, Barclay, Harris, Hoskins, and Kokot[3] showed by an X-ray examination of single crystals of the acetylacetonemono(*o*-hydroxyanil)copper(II) complex that the crystal structure was composed of dimeric molecules with the molecular structure shown in Figure 1. The temperature dependences of the magnetic susceptibilities of three related complexes were reported to be similar to that exhibited by copper acetate monohydrate.[3]

The mechanism by which the unpaired electrons on adjacent copper ions in the binuclear molecules pair their spins has not been elucidated. In their first paper Barclay, *et al.*,[3] suggested that the electron pairing occurred by superexchange through the bridging oxygens, but recently Barclay and Hoskins[4] have noted that a direct copper–copper interaction cannot be ignored. Since the copper–copper internuclear distance of 3.0 A in the compound shown in Figure 1 is intermediate between the 2.64 A found in copper acetate monohydrate[5] and the 3.3 A found in the binuclear pyridine

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[1] This work was supported by the North Carolina Board of Science and Technology, the National Science Foundation, and the Advanced Research Projects Agency, and was presented at the combined Southeast–Southwest Regional Meeting of the American Chemical Society at Memphis, Tenn., Dec 2–4, 1965.

[2] M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957).

[3] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

[4] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[5] J. N. van Niekerk and F. K. L. Schoening, *Nature*, **171**, 36 (1953); *Acta Cryst.*, **6**, 227 (1953).

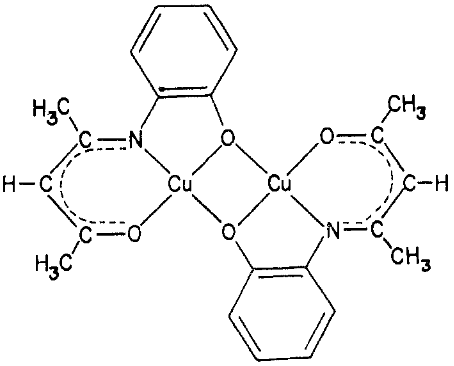
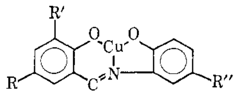


Figure 1.—The structure of the dimeric acetylacetone(mono-*o*-hydroxyanil)copper(II) complex.

N-oxide complex of copper(II) chloride,[6] no conclusion can be reached on the basis of internuclear distance. In copper acetate monohydrate, the direct metal–metal bond mechanism has been suggested many times,[7–11] and the evidence indicates that the spin–spin pairing occurs by superexchange in the dimeric copper chloride complex with pyridine N-oxide.[12] As a part of a program devoted to the magnetic properties of binuclear copper complexes, we have prepared several complexes with substituted tridentate Schiff's bases and have investigated their magnetic properties. In this paper we wish to present some of the results of our work which indicate that the system is complicated by the formation of isomers and by inter- as well as intramolecular magnetic interactions.

Table I

Analytical Data

Compound	R	R′	R″	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
	H	H	H	56.83	57.04	3.30	3.53	5.10	5.38
	Cl	H	H	50.50	50.44	2.61	2.91	4.53	4.73
	NO_2	H	H	48.83	49.05	2.52	2.78	8.76	8.89
	CH_3	H	H	58.23	58.50	3.84	4.04	4.85	4.74
	OCH_3	H	H	55.17	55.06	3.64	3.45		
	H	NO_2	H	48.83	48.90	2.52	2.67	8.76	8.49
	H	H	Cl	50.50	50.74	2.61	2.98	4.53	4.41
	H	H	C_6H_5	64.85	64.85	4.01	3.95	3.98	4.06

Experimental Section

Preparation of the Compounds.—The analytical data for the compounds prepared in this study are given in Table I. For simplicity and conciseness the compounds are denoted by a symbolic monomeric unit [R, R′, R″]. The compounds were prepared by the reaction of the Schiff's bases with copper acetate monohydrate in a 1:1 solution of ethanol and water. The reaction product was dissolved in pyridine, and the resulting solution was treated with a large excess of water, thereby yielding the monopyridine adduct with the general formula [Cu(Schiff base)-(py)]. The monomeric pyridine adduct was decomposed to the binuclear Schiff's base complex by heating it in boiling ethanol for approximately 1 hr. This is essentially Kishita's original method.[2] In addition, our samples were recrystallized from either bromobenzene or nitrobenzene. The crystalline powders resulting from Kishita's preparative procedure were dissolved in the boiling solvent, and the solution was concentrated, filtered, and placed while still hot in a large dewar flask. The crystalline powders which separated upon cooling were collected on a Büchner funnel, washed with ether to remove the high boiling solvent, and dried in a stream of air.

Magnetic Susceptibility Determinations.—Magnetic properties were determined as a function of temperature by the Faraday method using equipment and procedures which will be described elsewhere.[13] The equipment includes a Varian V4004 electromagnet and a Cahn Model GRAM electrobalance. Forces can be measured with a precision of at least 1.0 μg. For a 15-mg sample, the observed forces will range from approximately +200–300 μg at the Néel temperature to approximately −50 μg at low temperatures. Consequently, the precision of the experimental data is a complex function of temperature. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard.[14] Diamagnetic corrections were estimated from Pascal's constants.[15] Kishita, Muto, and Kubo[2] have demonstrated that the diamagnetic correction of 126 × 10^{-6} cgs unit for the Schiff's base salicyl-*o*-hydroxybenzylamine estimated from Pascal's constants agrees exactly with the measured diamagnetic susceptibility. This remarkable result confirms the utility of these constants for the purposes of this work. The molar magnetic susceptibilities calculated from the experimental data on the basis of the monomeric units listed in Table I are presented in Table II.

Characterization of the Compounds.—Powder patterns were recorded using nickel-filtered copper Kα X-radiation generated by a Norelco table-top generator and a 57.3-mm diameter Debye–Scherrer camera. The samples were contained in 0.5-mm diameter capillary tubes with a wall thickness of 0.01 mm. Powder patterns of all samples were different. Since the compounds were not isomorphous, it was not possible to assign structures on the basis of isomorphism.

Visible and ultraviolet spectra of solutions of the compounds in tetrahydrofuran were recorded with a Perkin-Elmer Model 202 spectrophotometer. Spectra of samples mulled in mineral oil were recorded at room temperature and at 77°K with a Cary Model 14 spectrophotometer.

Results

Magnetic Susceptibility Data.—The compounds can be classified into four classes according to their magnetic behavior. One compound, [H, H, Cl],[16] class I, exhibits normal paramagnetic behavior; one compound, class II, exhibits magnetic behavior similar to that of copper acetate monohydrate; one compound,

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(6) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(7) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(8) L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962).

(9) E. A. Boudreaux, *Inorg. Chem.*, **3**, 506 (1964).

(10) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057 (1959).

(11) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964), and other references therein.

(12) W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc.*, **86**, 3888 (1964).

(13) W. E. Hatfield, C. S. Fountain, and R. Whyman, to be published.

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(15) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 6.

(16) The compounds are denoted by the substituents in the order [R, R′, R″] given in Table I.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA

[CH_3, H, H]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
376	834	1.59[a]
359	854	1.57
347	856	1.55
334	862	1.52
313	907	1.51
300	912	1.49
298	923	1.49
289	958	1.49
284	955	1.47
267	954	1.43
260	957	1.42
240	957	1.36
220	954	1.30
200	947	1.23
180	938	1.16
160	881	1.07
120	609	0.75
98	408	0.57

[Cl, H, H]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
390	777	1.56[a]
380	786	1.60
368	799	1.54
358	805	1.52
348	824	1.52
335	820	1.49
326	820	1.47
320	817	1.45
308	814	1.42
298	811	1.40
290	811	1.38
282	808	1.35
269	795	1.31
262	785	1.20
249	768	1.24
241	774	1.22
220	712	1.12
200	653	1.03
180	607	0.94

[NO_2, H, H]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
373	789	1.54[a]
358	804	1.52
343	817	1.50
329	829	1.48
319	829	1.46
299	849	1.42
282	877	1.41
267	883	1.37
253	883	1.34
238	880	1.30
223	887	1.26
205	880	1.21
189	887	1.15
174	871	1.11
162	865	1.06
139	837	0.97
123	839	0.91
108	864	0.86
91	903	0.81

[OCH_3, H, H]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
384	1339	2.03[a]
374	1338	2.01
360	1351	1.98
346	1365	1.95
329	1374	1.91
312	1381	1.86
300	1383	1.82
271	1383	1.74
253	1377	1.68
229	1354	1.58
209	1324	1.49
193	1275	1.41
171	1218	1.30
145	1107	1.14
125	1024	1.02
95	923	0.84
90	978	0.84
84	1181	0.90

[H, H, C_6H_5]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
367	959	1.68[a]
351	970	1.66
334	993	1.63
313	1012	1.60
298	1008	1.56
273	1019	1.50
248	1021	1.43
225	1014	1.36
200	1003	1.27
176	1000	1.19
145	983	1.07

[H, NO_2, H]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units		μ_{eff}, BM
377	906[b]	903[c]	1.66[a]
349	937	936	1.62
332	960	956	1.60
310	983	981	1.57
299	997	993	1.55
288	1009	1004	1.53
280	1023	1011	1.52
268	1027	1021	1.49
261	1031	1026	1.47
250	1034	1032	1.44
240	1030	1035	1.41
220	1035	1033	1.31
200	1024	1017	1.28
180	983	979	1.19
160	902	912	1.08
120	545	655	0.73
100	380	466	0.55

[H, H, Cl]

T, °K	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}, BM
299	1462	1.87[a]
288	1504	1.87
280	1541	1.86
268	1558	1.83
260	1627	1.85
250	1690	1.84
240	1707	1.81
220	1779	1.78
200	1942	1.77
160	2274	1.71
140	2465	1.60
120	2818	1.65
98	3241	1.62

[a] Computed from $\mu_{eff} = 2.84(\chi_M^{cor}T)^{1/2}$. [b] Observed. [c] Calculated; see text.

class III, exhibits antiferromagnetism apparently complicated by factors to be discussed in a subsequent section; and finally, two compounds, class IV, exhibit magnetic behavior which suggests both intra- and intermolecular magnetic interactions. The magnetic data for these compounds are given in Table II. In additon to the compounds for which magnetic properties were determined over an extended temperature range, the behavior of the [Cl, H, H] and the [H, H, C_6H_5] compounds was determined in the region of the Néel temperatures. These data are given in Table II, also.

Spectral Properties.—All of the compounds exhibited a multicomponent band system covering the spectral range from 3500 to 5000 A. The band maxima and approximate energies of discernible shoulders are given in Table III. The data for a representative member from each class show that the band maxima are not significantly dependent upon temperature. The intensity of the lowest energy component of the band system exhibited a slight temperature dependence; it became measurably more intense, ~5%, upon cooling to 77°K.

TABLE III

SPECTRAL DATA[a]

Compound		Band maxima, cm^{-1}		Comments
[H, H, H]		23,200	22,000 sh	Soln in THF
[CH_3, H, H]	25,800 sh	23,200	21,900	Mull at room temp
	26,000 sh	23,400	21,900	Mull at 77°K
[NO_2, H, H]		23,300	21,800 sh	Soln in THF
	~28,000 sh	23,900	~22,000 sh	Mull at room temp
	27,800	23,900	~22,000 sh	Mull at 77°K
[OCH_3, H, H]		21,200	21,100 sh	Soln in THF
[Cl, H, H]		22,600		Soln in THF
[H, NO_2, H]		22,500		Soln in THF
[H, H, C_6H_5]		22,200	21,300	Soln in THF
[H, H, Cl]		22,600	21,600	Soln in THF
		23,300	22,000	Mull at room temp
		23,400	22,000	Mull at 77°K

[a] Abbreviations used in the table are: THF, tetrahydrofuran; sh, shoulder.

Discussion

Structure.—The crystal structure in Figure 1 determined by Barclay and Hoskins[4] shows that the oxygens from the aminophenol moieties serve as the bridging units. Additional isomeric forms can be visualized. In a second isomer one bridging oxygen comes from the aminophenol and the other from the enol function of the ligand. The third isomer could have both oxygens from the acetylacetones. The parent compound of this present study, [H, H, H], is closely related to the acetylacetone-*o*-hydroxyanil complex, and the corresponding isomers are shown in Figure 2.

Magnetic Properties.—First consider the [CH_3, H, H] compound. The molar magnetic susceptibility of this compound is constant at ~950 × 10^{-6} cgs unit over a temperature range of approximately 90°. Above 290°K the susceptibility decreases as the temperature increases and below 200°K the susceptibility decreases as the temperature decreases. Whereas the magnetic behavior as a function of temperature indicates antiferromagnetic behavior, the data do not conform to that expected from the theoretical expression[17]

$$\chi_M = \frac{g^2N\beta^2}{3kT}\left(1 + \frac{1}{3}\exp(-2J/kT)\right) + N\alpha \qquad (1)$$

where g is the Landé splitting factor, N Avogadro's number, β the Bohr magneton, k Boltzmann's constant, $-2J$ the splitting between the singlet and triplet states, and $N\alpha$ the temperature-independent paramagnetism. A value of 60 × 10^{-6} cgs unit per copper(II) ion was assumed for the temperature-independent paramagnetism. The above expression describes the temperature dependence of the magnetic susceptibility of an electronic system composed of a singlet state and a triplet state separated by an energy difference $-2J$. Magnetic systems whose properties can be described by the theoretical expression for χ_M usually exhibit a reasonably well-defined maximum. For example, over a comparable 100° temperature range for copper acetate monohydrate the susceptibility has decreased from its maximum value by ~20 × 10^{-6} cgs unit on the high-temperature side and by ~30 × 10^{-6} cgs unit on the low-temperature side. Although the accuracy of our experimental data is probably not within these limits, the precision is.

If it is assumed that intermolecular interactions are not operative in this system, then the data indicate that $|J|$ is not constant. It is not unlikely that the singlet–triplet splitting is a function of temperature. For example, Young and Murmann[18] have shown such to be the case for some binuclear copper(II)–α-amine oxime complexes. In addition to a temperature-dependent $|J|$, one could postulate that the behavior arises from a mixture of isomeric forms with unique singlet–triplet splittings of comparable magnitude.

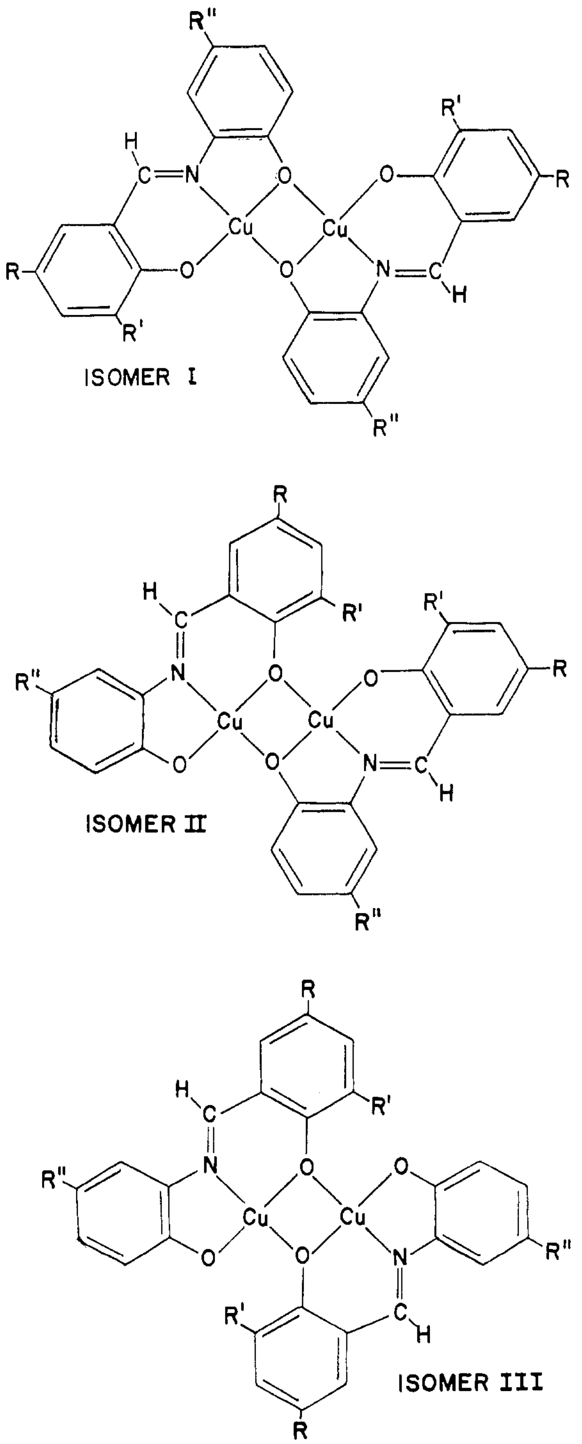

Figure 2.—Isomeric forms of the Schiff's base complexes.

If the mechanism of spin–spin coupling occurs by superexchange through the orbitals of the bridging oxygen atoms which do not participate in σ bonding, then the electron-donating properties of the methyl group would have little effect on $|J|$ (compared to [H, H, H]) for isomer I (Figure 2), but may have a noticeable effect for isomers II and III. Evidence for the existence of isomers has been obtained, but we have not been successful in our attempts to separate and characterize them. The relatively low solubility of the compounds augmented by their great affinity for available chromatographic column materials precludes

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(17) In order to conform with the most recent usage and with the usual definition of the exchange integral, the exponential term is given as $-2J/kT$ rather than J/kT.

(18) J. E. Young and R. K. Murmann, *J. Phys. Chem.*, **67**, 2647 (1963).

the use of fractional crystallization and chromatography for the separation problem.

In addition to the substituent effect anticipated on the basis of previous work with dimeric pyridine N-oxide complexes of copper halides,[12] it is conceivable that the isomers could have different crystal structures and different copper–oxygen and copper–copper bond distances. Structural changes of this type may mask the substituent effect, but would give rise to different $|J|$ values for the three isomers and result in a temperature dependence of molar magnetic susceptibility similar to that observed for [CH_3, H, H]. The copper–copper bond model can also be used to explain the data. Using this model, $|J|$ depends on both the copper–copper distance and the electronegativity of the bridging groups. Since the methyl group will undoubtedly affect the electron density about the bridging oxygen in isomers II and III, then it may be anticipated that the different isomers would have different bond distances and different singlet–triplet splitting energies.

The compound in class II exhibits copper acetate like behavior. In Table II the experimental data for the [H, NO_2, H] compound are compared with the theoretical data predicted using values for the g and $|2J|$ parameters of 2.19 and 259 cm^{-1}, respectively. For the purposes of fitting the experimental data to the theoretical curve, a GAT program was written for the UNIVAC 1105 computer. The program was written to give the best fit of all the reliable experimental data to the theoretical expression.

It is of interest to note why the data for [H, NO_2, H] are not complicated by an isomer effect. This is the only compound studied with a substituent in the R′ position. An examination of the isomeric forms depicted in Figure 2 will reveal the steric interaction which would arise between R′ and the ligand coordinated to the adjacent copper ions in isomers II and III. As a result it appears that only one isomer (I) is formed.

The data for the [H, H, Cl] compound are not easily explained. In Figure 3 the reciprocal of molar susceptibility is plotted *vs.* temperature, and it can be seen that the data conform approximately to the Curie–Weiss law with the best straight line intercepting the temperature axis at −31°K. Neither of the isomers in Figure 2 would be expected to be paramagnetic, yet the analytical data support the formulation of the compound as a member of this series. It is unfortunate that the substituted compounds did not form an isomorphous series so that anomalies of this type could be explained.

The magnetic behavior of the [H, H, Cl] compound is not observed for all compounds with substituents at R″. As the data in Table II indicate, the compound with a phenyl group substituted at R″ exhibits antiferromagnetism.

The data for the [OCH_3, H, H] and [NO_2, H, H] compounds are displayed in Figure 4. There are two features of the data which should be pointed out. The susceptibility of both compounds increases as the temperature decreases from about 380°K, reaches a maximum, and then decreases with temperature to about 100–120°K. At that point the susceptibility begins to increase rapidly. Our present equipment will not permit the investigation of this interesting behavior below ~80°K. A second interesting point is the magnitude of the susceptibility at the maximum for the [OCH_3, H, H] compound. All of the other compounds exhibited maximum molar susceptibilities approximately 300–500 × 10^{-6} cgs unit less than that of [OCH_3,H,H].

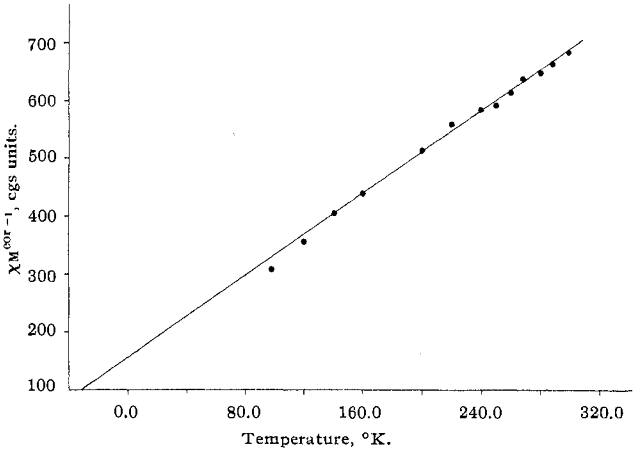

Figure 3.—The Curie–Weiss plot of the magnetic data for the [H, H, Cl] compound.

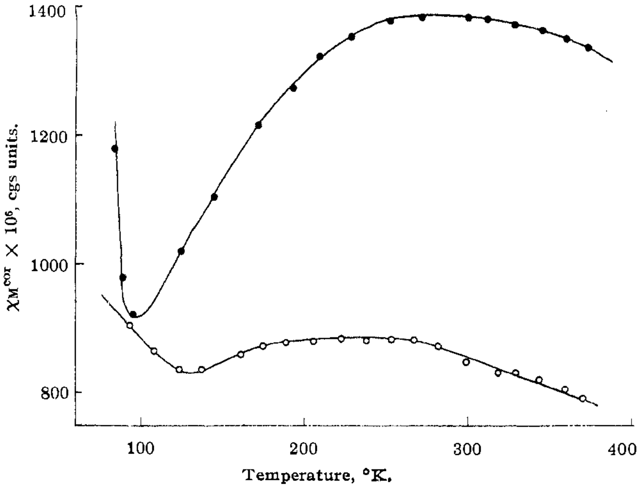

Figure 4.—The temperature dependences of the magnetic susceptibilities of the [OCH_3, H, H] and [NO_2, H, H] compounds: (●, [OCH_3, H, H]; ○, [NO_2, H, H]).

The crystal structure determination by Barclay and Hoskins[4] shows that the nearly planar molecules are stacked in the solid state so that a bridging oxygen atom from an adjacent dimer is positioned over a copper ion of the molecule in question, giving a distorted square-pyramidal geometry to that copper ion. The copper–oxygen bond distance is approximately 2.64 A, which is to be compared with the ~2.0 A copper–oxygen bond distance in the plane. The sixth coordination position of this copper ion and the fifth and sixth positions of its dimeric partner are occupied by carbon atoms at 3.13–3.36 A. Conceivably, intermolecular interactions could be transmitted through these linkages.

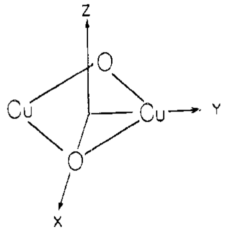

Figure 5.—The coordinate system used to construct the reducible representations.

Spectral Properties.—There are no features in the spectra of these magnetically anomalous compounds which would serve to differentiate them from compounds which exhibit normal magnetic properties. The absence of any marked temperature effect on intensities is similar to the behavior of copper acetate monohydrate. Tonnet, Yamada, and Ross[19] have qualitatively explained the absence of a temperature effect in the spectrum of copper acetate in terms of the coincidental energy differences between the low-lying singlet and triplet states and the corresponding excited states of the same multiplicities. Perhaps the same situation arises for this series of compounds. More likely, the crudity of the experiment has obscured any potentially interesting spectral features. The first coordination sphere of the two copper ions in the dimeric molecules are quite different, but the expected complex spectra are not observed; instead the spectra appear quite simple, perhaps due to the overlapping of a number of bands in the chromophoric region. In such a situation, a decrease in the intensity of one band accompanied by an increase in the intensity of a second band also lying under the apparent band envelope could not be detected by the mull technique.

Model for Superexchange.—Martin and Winter[20] have recently presented magnetic data for binuclear di-π-cyclopentadienyltitanium(III) chloride and have discussed the results in terms of multicentered bonding. This model is consistent with the data for these binuclear Schiff's base complexes of copper and will be presented here.

The $\mathrm{Cu}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{Cu}$ unit illustrated in Figure 5 has nearly D_{2h} symmetry.[4] Assuming that the copper σ bonds use mainly the $3d_{xy}$, 4s, and $4p_{\pm 1}$ orbitals, then the remaining 3d orbitals and the $4p_z$ orbitals on the copper ions are mostly nonbonding or π bonding. Inspection of the molecular structure reveals a considerable departure from the 120° angle expected for an sp^2-hybridized oxygen atom bridging the two copper ions.[4] The observed angle of 102° probably represents a compromise in distortion since the 120° bond angle would require a considerable compression of the copper bonding orbitals. In this model the $2p_z$ orbitals of the bridging oxygen atoms which are normal to the nearly planar molecule are used in the exchange mechanism. These two $2p_z$ orbitals form a representation of the group D_{2h} which transforms as $b_{2g} + b_{1u}$, and the sets of metal $4p_z$, $3d_{xz}$, and $3d_{yz}$ also span representations which contain b_{2g} and b_{1u}. Therefore, the multicentered bonding may arise from an interaction between the $4p_z$, $3d_{xz}$, and $3d_{yz}$ orbitals of the copper ions with the $2p_z$ orbitals on the bridging oxygen atoms in the manner shown for the π orbitals in Figure 6.

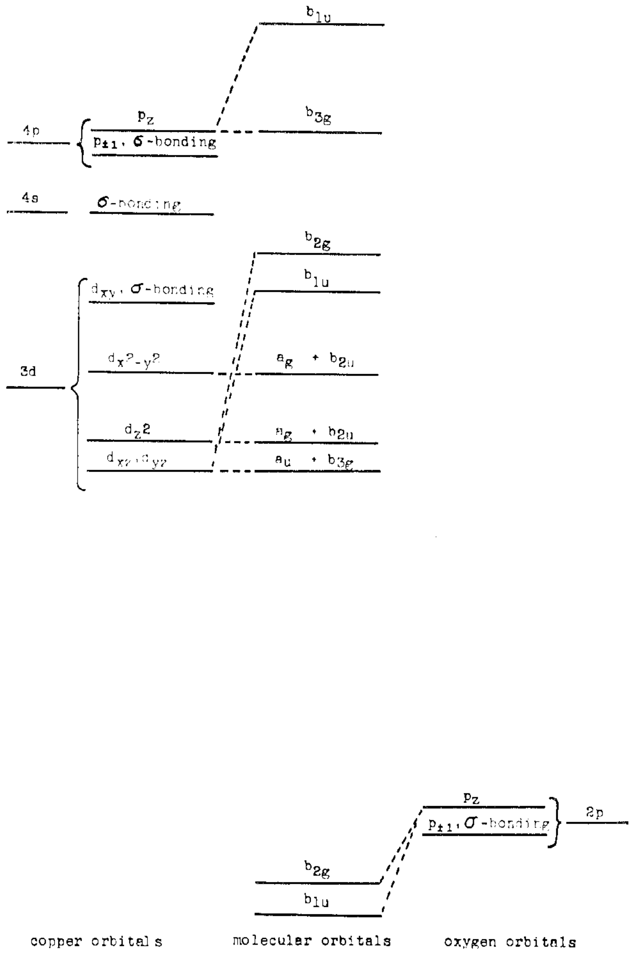

Figure 6.—A schematic molecular orbital diagram for the CuO-CuO unit (not drawn to scale).

In the construction of Figure 6 the splitting of the copper atomic orbitals was assumed to be of a magnitude comparable to that resulting from previous molecular orbital treatments of copper complexes,[21] and, further, the d orbitals were assumed to be split by the ligand atoms in the manner given by Basolo and Pearson[22] for a square-planar complex.[23] The splitting between the bonding and antibonding levels of a given symmetry was taken to be proportional to the atomic overlap. Therefore, the qualitative ordering of energy levels in Figure 6 must be regarded as tentative until a detailed calculation is performed. Nevertheless, Figure 6 illustrates that the 22 mostly nonbonding and π bonding electrons fill the orbitals up through the b_{3g} molecular orbital giving a configuration of $[\ldots(b_{3g})^2]$ with symmetry ^1A_g for the ground state.

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[19] M. L. Tonnet, S. Yamada, and I. G. Ross, *Trans. Faraday Soc.*, **60**, 840 (1964).

[20] R. L. Martin and G. Winter, *J. Chem. Soc.*, 4709 (1965).

[21] W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, **4**, 1181 (1965).

[22] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 55.

[23] Note the change in the labeling of the coordinate system from ref 22.

The first excited state has a configuration [. . . $(b_{3g})(b_{1u})$] with symmetry B_{2u}.

Substituents on the chelate rings which remove electron density from the p_z orbitals of the bridging oxygen atoms decrease the b_{3g}–b_{1u} energy difference, give rise to molecules with destabilized singlet states, and consequently lower singlet–triplet splitting energies. Similarly, substituents which donate electron density increase the b_{3g}–b_{1u} splitting, stabilize the singlet state, and give rise to higher $|J|$ values.

Conclusions.—The following conclusions may be drawn from this study. The nature of the substituent and its relative position on the ligand greatly affect the magnetic properties of the dimeric compounds, and the effect is both electronic and steric in nature. Because of the complications, the data do not unambiguously support either mechanism of spin–spin coupling. However, the data for the [Cl, H, H] compound are very difficult to explain within the framework of the metal–metal bond model, since on the basis of this model, the singlet–triplet splitting energy should be equal to or lower than that observed for the unsubstituted compound with the same structure. That is not the case for [Cl, H, H]; the Néel temperature for the sample of this compound was approximately 80° higher than that of the unsubstituted compound.

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Complexes of Cobalt(II). I. On the Anomalous Magnetic Behavior of Some Six-Coordinate Cobalt(II) Complexes

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The average magnetic susceptibilities of ten related, six-coordinate microcrystalline cobalt (II) compounds have been determined between 100 and 500°K. One of these complexes is of the normal high-spin variety; nine exhibit room temperature magnetic moments lying below the range of values customarily found for high-spin, six-coordinate cobalt(II) systems but above that characterizing the low-spin systems. Six of the complexes having intermediate room temperature magnetic moments exhibit "anomalous" Curie–Weiss behavior. The observed behavior of the anomalous complexes is interpreted in terms of a Boltzmann distribution over thermally accessible levels characterized by different spin multiplicities. These six complexes provide the first examples of this type of behavior reported for cobalt(II) complexes.

Introduction

The six-coordinate complexes of cobalt(II) are usually high-spin with magnetic moments near 5 BM,[1,2] reflecting a large orbital contribution to the magnetic moment. The few six-coordinate, low-spin cobalt(II) complexes reported in the literature exhibit moments only slightly larger than the spin-only value of 1.7 BM, *viz.*, 1.9–2.0 BM.[1] Application of the crystal field theory leads one to expect that the octahedral complexes of a d^7 ion such as cobalt(II), formed by using an extended series of ligands having a sufficiently wide range of ligand field strengths, would be high-spin at the low-field limit and low-spin at the high-field limit. But, within a relatively small range of field strengths somewhere between the two extremes, the two states are expected to have comparable stabilities.[3]

Relevant data are rare, although there has been considerable speculation concerning the existence of a Boltzmann distribution of states characterized by more than one spin multiplicity in certain complexes with anomalous magnetic moments.[4–18]

A survey of values for the room-temperature magnetic moments of cobalt(II) complexes, presumably of coordination number six, reveals the existence of essentially no gaps in room temperature moment from about 1.8 to 5.2 BM,[16] and a number of those in the intermediate range must be considered unusual even when allowance is made for the partially quenched orbital angular momentum.

Intermediate room-temperature magnetic moments of cobalt(II) complexes could arise as a consequence of a combination of, or one of, the following: (1)

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(1) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

(2) B. N. Figgis, *Nature*, **182**, 1569 (1958).

(3) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

(4) L. Cambi and L. Szego, *Ber.*, **66B**, 656 (1933).

(5) A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Australian J. Chem.*, **17**, 294 (1964).

(6) J. H. M. Thornley, C. G. Windsor, and J. Owen, *Proc. Roy. Soc.* (London), **A284**, 252 (1965).

(7) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964).

(8) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).

(9) R. H. Holm and T. M. McKinney, *ibid.*, **82**, 5506 (1960).

(10) R. H. Hohn, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).

(11) L. E. Orgel, *J. Chem. Phys.*, **23**, 1818 (1955); "Some Applications of Crystal Field Theory to Problems in Transition Metal Chemistry," Report to the Xth Solvay Council, Brussels, May 1956.

(12) M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1946).

(13) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(14) L. Sacconi, R. Cini, J. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(15) R. C. Stoufer, W. B. Hadley, and D. H. Busch, *ibid.*, **83**, 3732 (1961).

(16) D. H. Busch, "Cobalt," R. S. Young, Ed., American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

(17) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 229 (1956).

(18) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Trans. Faraday Soc.*, **26**, 72 (1958).