3) at 2.2-Å internuclear distance, but only 0.095 between Co and Se ($n = 4$) after allowing for the larger atomic radius of Se). A possible explanation could be reached on the assumption that π back-donation, lowering the energy of dπ orbitals, occurs to a larger extent with Se than with S ligands.

The nephelauxetic effect estimated from the energy difference between the first two d–d bands of Cr(dsc)$_3$ and the first two of Co(dsc)$_3$ yields $\beta_{35} = 0.41$ in the former and 0.36 in the latter case. These are remarkably low values, in agreement with previous reports that selenium donors are able to cause a much more pronounced nephelauxetic decrease than the corresponding sulfur-containing ligands.[1]

Determination of the optical electronegativity of dsc$^-$ is uncertain because of the difficulty of assigning exactly the charge-transfer bands in the presence of intense ligand bands. Probably the best guess can be made from the spectrum of Co(dsc)$_3$, which has a charge-transfer band at 22.2 kK, corresponding, after the correction $(-\Delta + D)$, to a σ_{cor} value of 9.9 kK; *i.e.* $\chi_{\text{opt}}(\text{dsc}^-) \sim 2.68$ if we assume $\chi_{\text{opt}}(\text{Co}) = 2.35$.[20]

Identification of the true charge transfer $\pi \rightarrow e_g$ is very uncertain in the complex spectrum of the Cr(III) compound. The charge transfer at 26.1 kK in Pd(dsc)$_2$, if compared with the first charge transfer of $[\text{PdBr}_4]^{2-}$ at 30.2 kK and of $[\text{PdI}_4]^{2-}$ at 20.5 kK, leads to χ_{opt} (dsc) $\sim$ 2.6. Thus all data point, although somewhat unclearly, to an χ_{opt} of Se in dsc$^-$ between 2.6 and 2.7, almost imperceptibly lower than that of S in dtc$^-$ (2.7 according to ref 21). In a parallel comparison, $\chi_{\text{opt}} = 2.7$ for $(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ and 2.6 for $(\text{C}_2\text{H}_5\text{O})_2\text{PSe}_2^-$, the difference in χ_{opt} between S and Se is already small (0.1). Here it is even smaller, and in our opinion they might be a consequence of extensive π bonding between metal and ligand, including also π back-donation and resulting in a lowering of the filled π orbitals of the ligands.

(20) C. K. Jørgensen, *Mol. Phys.*, **6**, 43 (1963).

(21) C. K. Jørgensen, "Inorganic Complexes," Academic Press Inc., New York, N. Y., 1963, p 137.

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
THE UNIVERSITY OF NEW SOUTH WALES, SYDNEY, AUSTRALIA

Metal Complexes as Chelates. II. Binuclear Complexes Containing Similar and Dissimilar Metal Atoms[1]

BY S. J. GRUBER, C. M. HARRIS, AND E. SINN

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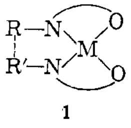
A new series of oxygen-bridged complexes is reported with special emphasis on copper(II). Most of these complexes can be shown to be discrete dimeric molecules. Both homo- and heteronuclear dimers can be prepared in a large number of cases, by forming a complex of metal M with a tetradentate salicylaldimine, L, and, in turn, using this complex itself as a ligand. The latter (ML) then acts as a bidentate in complexing with a metal halide, MX$_2$ or M'X$_2$, to which it coordinates through its two phenolic oxygens. The Schiff base complexes used here as ligands ("complex ligands") are tetradentate Schiff base complexes of copper(II) and nickel(II). The former are normal paramagnetics, in contradistinction to reports of anomalous magnetic moments, and the latter are well known to be diamagnetic. The binuclear complexes are generally considerably less soluble in organic solvents than the complex ligands, so that many different complexes can be formed by direct reaction in saturated solutions. Both the complex ligands and the binuclear complexes are nonionic in nitrobenzene. All of the homonuclear complexes of copper(II) show antiferromagnetic interactions, which can readily be explained in terms of the well-established "Bleany–Bowers" theory. Heteronuclear complexes so far prepared involving copper(II) with other paramagnetic and diamagnetic metals and nickel(II) with other paramagnetic metals are simple paramagnetics and their magnetic properties are in accord with the Curie–Weiss law, between 80 and 400°K, with relatively small Weiss constants.

Introduction

Solutions of various metal salicylaldimines (1) and metal halides reacted in organic solvents to form new types of complexes to which we attribute an oxygen-bridged structure (2). In this way it is possible to bring almost any two metals, similar and dissimilar, into combination.[1,2] Various types of trinuclear complexes involving both similar and dissimilar metals, were prepared using an analogous method, but with noncoordinating anions such as perchlorate replacing the halogen atoms.[1,2] Oxygen bridging of the type shown in structure 2 brings groups of two or three metal atoms into close proximity so that antiferromagnetic interactions occur in a number of cases where the metals have unpaired electrons. The shifts observed in the infrared frequencies associated



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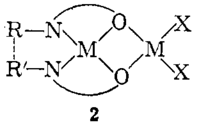

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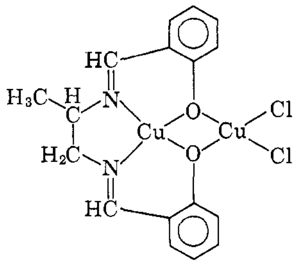
[1] (a) Part I: S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Letters*, **3**, 496 (1967); (b) taken in part from the Ph.D. thesis of S. J. Gruber, University of New South Wales, 1966. Preliminary work was reported in the B.Sc. (Honors) thesis of S. J. Gruber, 1962.

[2] S. J. Gruber, C. M. Harris, and E. Sinn, to be published.

with the bonds to the oxygen atoms in the salicylaldimines are under investigation.

In this paper, we are concerned with: (a) copper(II) and nickel(II) derivatives of the tetradentate Schiff base, N,N′-ethylenebis(salicylideneimine), ES; N,N′-1,3-propylenebis(salicylideneimine), 1,3-PS; N,N′-1,-2-propylenebis(salicylideneimine), 1,2-PS; N,N′-*o*-phenylenebis(salicylideneimine), PS; N,N′-4-methyl-*o*-phenylenebis(salicylideneimine), MPS; N,N′-ethylenebis(*o*-hydroxyacetophenylideneimine), EHA; N,-N′-1,3-propylenebis(*o*-hydroxyacetophenylideneimine), 1,3-PHA; and (b) the complexes, such as [(Cu-1,2-PS)$\mathrm{CuCl_2}$] (**3**), dichloro(N,N′-1,2-propylenebis(salicylideneiminato)copper(II))copper(II), formed when these copper(II) and nickel(II) derivatives are used as ligands.



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Tetradentate Schiff bases of the type used here have long been known, as have their simple metal complexes.[3,4] N,N′-Ethylenebis(salicylideneiminato)copper(II) (CuES) is dimeric in the solid state, with the copper atom of one monomeric unit linked to one of the phenolic oxygens of the other unit, but this bond (2.4 Å) is much weaker than the four bonds of each copper with its own tetradentate base (average 2.0 Å).[5,6] This linkage is unlikely to lead to any significant antiferromagnetic interaction, as no such interaction has been observed in any copper complexes of this type where the bridge contained so weak a copper–oxygen bond; in the way of a possible exception to this are the low magnetic moments reported[7a] for some tetradentate salicylaldimine complexes of copper(II), but these results are in disagreement with those presented below and with the more recent results of Lewis and Walton.[7b]

Oxygen-bridged structures readily form in many nickel(II) salicylaldimine complexes, both in the solid[8] and in solution,[9] and the nickel complexes can become paramagnetic by raising the coordination number of the metal from four to five or six. Dimerization or polymerization *via* bridging oxygens can also occur in salicylaldimines of other metals, such as zinc.[10] The frequent occurrence of this type of linkage demonstrates the readiness with which two-coordinate oxygen in this kind of compound can raise its coordination number to three, the property upon which the formation of our binuclear complexes is based.

Experimental Section

Preparation and Analysis.—The organic ligands and their metal complexes were prepared as prescribed by earlier workers,[3,4] and analytical data are given in Tables I and II. As the binuclear compounds are reported here for the first time, an intensive analytical investigation was undertaken.

TABLE I

ANALYTICAL DATA FOR SCHIFF BASES

Schiff base	Empirical formula	Analyses, % Calcd C	H	N	Found C	H	N
ES	$C_{16}H_{16}N_2O_2$	71.7	6.0	10.5	71.6	5.9	10.3
PS	$C_{20}H_{16}N_2O_2$	75.9	5.1	8.9	76.0	5.1	8.7
MPS	$C_{21}H_{18}N_2O_2$	76.3	5.5		86.3	5.6	
EHA	$C_{18}H_{20}N_2O_2$	73.0	6.8	9.5	72.9	6.7	9.4
1,3-PHA	$C_{19}H_{22}N_2O_2$	73.5	7.2	9.0	73.7	7.2	9.0

Copper was determined by reduction with potassium iodide followed by titration with 0.025 *N* sodium thiosulfate to a starch–iodine end point.

Nickel was determined gravimetrically as the dimethylglyoxime complex. Copper and cobalt, which interfere in this analysis, were removed by precipitation with hydrogen sulfide in acid solution or with α-nitroso-β-naphthol, respectively.

Cobalt was determined gravimetrically by precipitation with pyridine and ammonium thiosulfate. Copper was removed as sulfide in acid solution. In the presence of nickel the cobalt was isolated as the α-nitroso-β-naphthol complex. This complex was then destroyed with boiling nitric, perchloric, and sulfuric acids and the cobalt was determined in the usual way.

Zinc was determined gravimetrically as its ammonium phosphate. Copper was removed as sulfide by precipitation with hydrogen sulfide in acid soluton and nickel was removed in the form of its dimethylglyoxime complex where necessary.

Dichloro(N,N′-ethylenebis(salicylideneiminato)copper(II)copper(II) Monohydrate.—To a solution of CuES (3.3 g) in chloroform (900 ml) was added a solution of copper(II) chloride dihydrate (1.8 g) in ethanol (30 ml). A red precipitate was formed (yield 3.0 g). *Anal.* Calcd for $C_{16}H_{16}N_2O_3Cl_2Cu_2$: C, 39.8; H, 3.1; N, 5.8; Cu, 26.4. Found: C, 39.9; H, 3.1; N, 5.8; Cu, 26.4.

Dichloro(N,N′-propylenebis(salicylideneiminato)copper(II))-copper(II).—To a saturated chloroform solution of Cu-1,3-PS (3.44 g) was added slowly and with stirring a solution of copper(II) chloride dihydrate (1.8 g) in a minimum of ethanol. The solution was heated to boiling, whereupon a red crystalline precipitate was obtained. *Anal.* Calcd for $C_{17}H_{16}N_2O_2Cl_2Cu_2$: C, 42.6; H, 3.4; N, 5.9; Cu, 26.6. Found: C, 42.6; H, 3.4; N, 5.8; Cu, 26.4.

Dichloro(N,N′-1,2-propylenebis(salicylideneiminato)copper-(II))copper(II).—The compound was obtained in the form of red crystals by treating a solution of Cu-1,2-PS (3.4 g) in chloroform (300 ml) with an alcoholic solution (30 ml) of copper(II) chloride dihydrate (1.8 g). On mixing the two solutions a color change from dark blue to dark red was observed. After boiling for some minutes a red precipitate formed (yield 3.7 g). *Anal.* Calcd for $C_{17}H_{16}N_2O_2Cl_2Cu_2$: C, 42.6; H, 3.4; N, 5.9; Cu, 26.6. Found: C, 42.8; H, 3.6; N, 5.8; Cu, 26.4.

Dichloro(N,N′-1,3-propylenebis(*o*-hydroxyphenylideneiminato)-copper(II))copper(II) Monohydrate.—Cu-1,3-PHA (2.0 g) in chloroform (200 ml) was treated with an ethanolic solution

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(3) J. U. Dubsky and A. Sokol, *Collection Czech. Chem. Commun.*, **3**, 548 (1931).

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(5) M. von Stackelberg, *Z. Anorg. Chem.*, **253**, 136 (1947); B. Meuther and M. von Stackelberg, *ibid.*, **305**, 279 (1960).

(6) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

(7) (a) C. H. Barklew and M. Calvin, *J. Am. Chem. Soc.*, **68**, 2261 (1946); (b) J. Lewis and R. A. Walton, *J. Chem. Soc., Sect. A*, 1559 (1966).

(8) C. M. Harris, S. L. Lenzer, and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958); **14**, 420 (1961).

(9) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961); R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962); A. H. Ewald and E. Sinn, *ibid.*, **6**, 40 (1967).

(10) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966), and references given.

Table II

Analytical Data for Schiff Base Complexes Used as Ligands

Complex	Empirical formula	Color	Analyses, %							
			Calcd				Found			
			C	H	N	Metal	C	H	N	Metal
CuES	$C_{16}H_{14}N_2O_2Cu$	Green	58.3	4.3	8.5	19.3	58.5	4.2	8.4	19.7
Cu-1,3-PS	$C_{17}H_{16}N_2O_2Cu$	Green	59.4	4.7	8.2	18.5	59.4	4.7	8.2	18.2
Cu-1,2-PS	$C_{17}H_{16}N_2O_2Cu$	Blue	59.4	4.7	8.2	18.5	59.8	4.8	8.2	18.3
CuEHA	$C_{18}H_{18}N_2O_2Cu$	Red needles	60.4	5.1	7.8	17.8	59.5	5.4	8.1	19.3
Cu-1,3-PHA	$C_{19}H_{20}N_2O_2Cu$	Green crystals	61.4	5.4	7.5	17.1	61.6	5.4	7.4	17.1
$CuPS\cdot CHCl_3$	$C_{20}H_{14}N_2O_2Cu\cdot CHCl_3$	Blue-black crystals	50.7	3.0	5.6	12.8	50.7	2.9	5.9	12.8
CuPS	$C_{20}H_{14}N_2O_2Cu$	Brown	63.6	3.7	7.4	16.8	63.6	3.7	7.5	16.6
CuMPS	$C_{21}H_{16}N_2O_2Cu$	Brown	64.4	4.1	7.2		64.5	4.2	7.0	
NiES	$C_{16}H_{14}N_2O_2Cu$	Red	59.1	4.3	8.7	18.1	58.8	4.3	8.7	18.0

(40 ml) of copper(II) chloride dihydrate. A red precipitate was obtained (yield 2.8 g). *Anal.* Calcd for $C_{19}H_{22}N_2O_3Cl_2Cu_2$: C, 43.5; H, 4.2; N, 5.3; Cu, 24.2. Found: C, 43.5; H, 4.2; N, 5.1; Cu, 23.8.

Dichloro(N,N′-ethylenebis(*o*-hydroxyacetophenylideneiminato)-copper(II))copper(II).—To a saturated chloroform solution of CuEHA was added an alcoholic solution of copper(II) chloride dihydrate in the ratio of 1:1. The volume of the solution was reduced considerably on a water bath, whereupon a blue-black crystalline precipitate was formed. *Anal.* Calcd for $C_{18}H_{18}N_2O_2Cu_2$: C, 43.9; H, 3.7; N, 5.7; Cu, 25.8. Found: C, 43.8; H, 3.7; N, 5.9; Cu, 25.6.

Dichloro(N,N(-*o*-phenylenebis(salicylideneiminato)copper(II))-copper(II) Monohydrate.—A solution of copper(II) chloride dihydrate (1.7 g) in alcohol (70 ml) was added dropwise to a solution of CuPS (3.78 g) in chloroform (500 ml). A very fine yellow-brown precipitate formed. The product was dried in an air oven at 100° (yield 3.8 g). *Anal.* Calcd for $C_{20}H_{16}N_2O_3Cl_2Cu_2$: C, 45.3; H, 3.0; N, 5.3; Cu, 24.0; Cl, 13.4. Found: C, 45.2; H, 3.1; N, 5.2; Cu, 23.5; Cl, 13.8.

Dichloro(N,N′-4-methyl-*o*-phenylenebis(salicylideneiminato)-copper(II))copper(II) Monohydrate.—Prepared analogously to the above compound. *Anal.* Calcd for $C_{21}H_{18}N_2O_3Cl_2Cu_2$: C, 46.3; H, 3.3. Found: C, 46.4; H, 3.3.

Dibromo(N,N′-*o*-phenylenebis(salicylideneiminato)copper(II))-copper(II) Hemihydrate.—A chloroform solution of CuPS (3.78 g) was treated with a solution of copper(II) bromide (2.33 g) in absolute alcohol (60 ml). The solution turned green and a fine green precipitate formed (yield 6.5 g). *Anal.* Calcd for $C_{20}H_{15}N_2O_{2.5}Br_2Cu_2$: C, 39.4; H, 2.5; N, 4.6; Cu, 20.8; Br, 26.2. Found: C, 39.3; H, 2.3; N, 4.7; Cu, 20.8; Br, 27.1.

Dibromo(N,N(-*o*-phenylenebis(salicylideneiminato)copper(II))-copper(II) Monohydrate.—The above preparation was repeated and the mixture allowed to stand until the initial green precipitate changed over a period of some minutes to a brown powder. The product was dried at 110° (yield 6.0 g). *Anal.* Calcd for $C_{20}H_{16}N_2O_3Br_2Cu_2$: C, 38.8; H, 2.6; N, 4.5; Cu, 20.5; Br, 25.8. Found: C, 39.0; H, 2.6; N, 4.4; Cu, 20.2; Br, 25.1.

Dichloro(N,N′-ethylenebis(salicylideneiminato)copper(II))cobalt(II).—To a solution of CuES (3.3 g) in chloroform was added a solution of cobalt(II) chloride hexahydrate (2.4 g) in a minimum of ethanol. An immediate reaction took place and a blue crystalline precipitate was formed (yield 2.3 g). *Anal.* Calcd for $C_{16}H_{14}N_2O_2Cl_2CuCo$: C, 41.9; H, 3.1; N, 5.1; Cu, 13.8; Co, 12.8. Found: C, 41.8; H, 3.1; N, 5.0; Cu, 13.7; Co, 12.6.

Dichloro(N,N′-ethylenebis(salicylideneiminato)nickel(II))-cobalt(II).—A solution of cobalt chloride hexahydrate (2.4 g) in ethanol (40 ml) was added slowly to a solution of NiES (3.24 g) in chloroform (300 ml). A dark olive-green precipitate formed. *Anal.* Calcd for $C_{16}H_{14}N_2O_2Cl_2NiCo$: C, 42.3; H, 3.1; N, 6.2; Ni, 12.9; Co, 13.0. Found: C, 41.9; H, 3.2; N, 6.4; Ni, 12.7; Co, 12.7.

Dichloro(N,N′-*o*-phenylenebis(salicylideneiminato)copper(II))-mercury(II).—A solution of mercury(II) chloride (2.72 g) in alcohol (70 ml) was added with stirring to a solution of CuPS (3.78 g) in chloroform (450 ml). An immediate reaction took place and the yellow precipitate formed was dried in an air oven at 105° (yield 6.6 g). *Anal.* Calcd for $C_{20}H_{14}N_2O_2Cl_2CuHg$: C, 37.0; H, 2.2; N, 4.3; Cu, 9.8; Cl, 10.9. Found: C, 37.0; H, 2.3; N, 4.1; Cu, 9.8; Cl, 10.9.

Dichloro(N,N(-*o*-phenylenebis(salicylideneiminato)copper(II))-zinc(II) Hemihydrate.—To a solution of CuPS (3.78 g) in chloroform (700 ml) was added a solution of zinc chloride in ethanol in slight excess. The yellow powder was dried at 105° (yield 4.2 g). *Anal.* Calcd for $C_{20}H_{15}N_2O_{2.5}Cl_2CuZn$: C, 45.9; H, 2.9; N, 5.4; Cu, 12.2; Zn, 12.7. Found: C, 45.4; H, 2.9; N, 5.3; Cu, 12.2; Zn, 12.6.

Magnetic Measurements.—Magnetic susceptibilities, χ_M, were determined on two Gouy balances, both of which have been described elsewhere,[11,12] and diamagnetic corrections were estimated from Pascal's constants. For the antiferromagnetic complexes, and for them only, the magnetic moments (Table III) were corrected for $N\alpha$, using the relation

$$\mu_{\text{eff}} = 2.828\sqrt{(\chi_M - N\alpha)T} \qquad (1)$$

where $N\alpha = 60 \times 10^{-6}$ cgs unit and is defined later in eq 2.

Table III

Magnetic Moments[a] of Complex Ligands and Magnetically Normal Binuclear Complexes

	μ_{cor}, BM	θ, °K	Temp range studied,[c] °K		μRT, BM	Temp, °K
CuES	1.90	−13.5	81–443	Cu-1,2-PS	1.81	297
Cu-1,3-PS	1.86	−7	83–354	$CuPS\cdot CHCl_3$	1.82	291
CuPS	1.81	+2	85–337			
CuMPS	1.84	+5	83–354			
$(CuPS)HgCl_2$	1.94	−4	84–364			
$(NiES)CoCl_2$	4.92	+9	82–423			
$(CuES)CoCl_2$	5.05[b]	−6.5	89–452			

[a] Per copper. [b] Per mole of binuclear complex; if μ_{cor}(Cu) is taken as 1.9 BM, μ_{cor}(Co) = 4.7 BM. [c] The detailed magnetic results over the temperature ranges specified in the table have been posted as Document No. 9692 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Results and Discussion

The copper compounds of general formula $[(CuL)CuX_2]\cdot nH_2O$, where n = 1 or 0, are all very slightly soluble in ethanol, acetone, methanol, and nitrobenzene. They are all nonelectrolytes in nitrobenzene solution,

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[11] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

[12] E. Sinn, M.Sc. Thesis, University of Sydney, 1966. We thank Dr. A. H. Ewald for permission to use this apparatus.

as are the tetradentate Schiff base complexes used as ligands ("complex ligands").

The moments (μ_{cor}) of the magnetically normal compounds, corrected for θ, or the room temperature moments (μ_{RT}) are given in Table III. These include the heteronuclear oxygen-bridged complexes as well as the complex ligands containing copper. It can be seen that the complex ligands are magnetically normal and obey the Curie–Weiss law with relatively small values of θ, where θ is defined by the relation $\chi_M \alpha [1/(T + \theta)]$. There is no evidence of any significant amount of antiferromagnetism.

The magnetic properties of the complexes $[(CuL)CuX_2] \cdot nH_2O$ are characteristic of pairwise antiferromagnetic interactions found in binuclear copper(II) complexes, and the results have been fitted to the "Bleany–Bowers" equation[13]

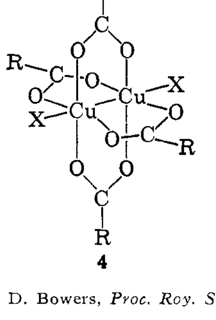
$$\chi_M = \frac{Ng^2\beta^2}{3kT}\,\frac{3e^{2J/kT}}{1 + 3e^{2J/kT}} + N\alpha \qquad (2)$$

with the aid of an IBM 1620 computer. $N\alpha$ was assumed to be 60 × 10^{-6} cgs unit. The values of best fit for J and g are given in Table IV, and some of the results are shown graphically in Figure 1. In general the magnetic properties of $[(CuL)CuX_2] \cdot nH_2O$ are well explained by this model of the pairwise antiferromagnetic interaction and are therefore powerful evidence for a binuclear structure in these compounds. With the exception of two compounds, $[(CuEHA)CuCl_2]$ and $[(CuPS)CuBr]_2 \cdot {}^1/_2H_2O$, the values of g obtained are in the range 2.10 ± 0.05, which may be compared with the range 2.15 ± 0.08 observed in the binuclear copper(II) alkanoates[14]

TABLE IV
MAGNETIC CONSTANTS FOR THE COMPOUNDS
$[(CuL)CuX_2] \cdot nH_2O$

	g	$2J$ Cm⁻¹	 Cal/mole	Temp range[a] studied, °K
$[(CuES)CuCl_2 \cdot H_2O$	2.11	232	663	80–377
$(Cu\text{-}1,3\text{-}PS)CuCl_2$	2.14	98	280	81–424
$(Cu\text{-}1,2\text{-}PS)CuCl_2$	2.15	212	606	81–354
$[(CuPS)CuCl_2] \cdot H_2O$	2.07	194	555	82–412
$[(CuMPS)CuCl_2] \cdot H_2O$	2.08	181	518	91–341
$(CuEHA)CuCl_2$	2.35	472	1350	81–423
$[(Cu\text{-}1,3\text{-}PHA)CuCl_2] \cdot H_2O$	2.05	280	801	86–363
$[(CuPS)CuBr_2] \cdot {}^1/_2H_2O$	2.28	388	1110	87–404
$[(CuPS)CuBr_2] \cdot H_2O$	2.09	190	543	82–396

[a] See footnote c, Table III.



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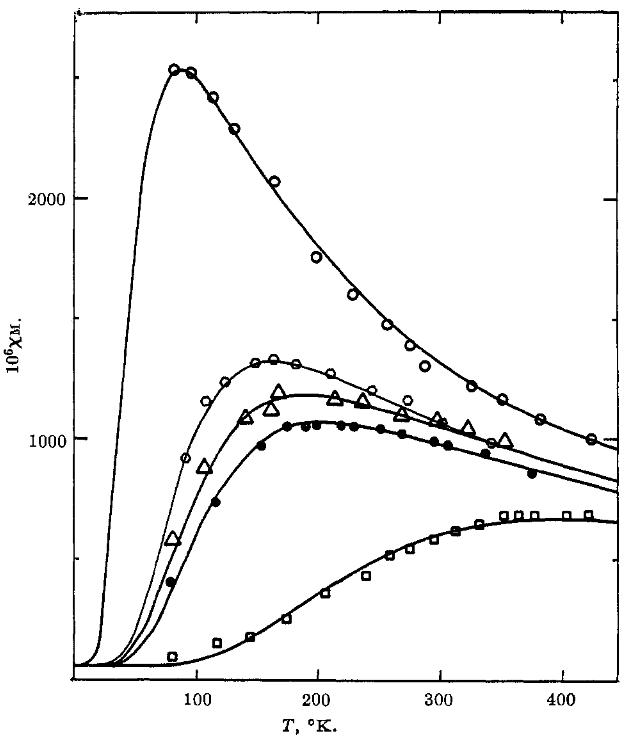
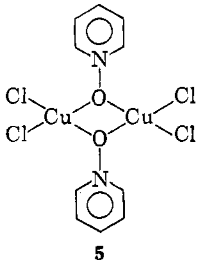


Figure 1.—The variation of magnetic susceptibility with temperature for the complexes $[(CuL)CuX_2] \cdot nH_2O$. The curves are calculated from eq 2 using the values of J and g given in Table V. Experimental values are denoted as: ○, $(Cu\text{-}1,3\text{-}PS)CuCl_2$; ○, $[(CuMPS)CuCl_2] \cdot H_2O$; △, $(Cu\text{-}1,2\text{-}PS)CuCl_2$; ●, $[(CuES)CuCl_2] \cdot H_2O$; □, $(CuEHA)CuCl_2$.

No definite trend is observed in the values of the singlet–triplet separations ($-2J$) which are of the order of magnitude of those in copper(II) alkanoates.[14] Similar magnetic properties were observed in pyridine and quinoline N-oxide[15] and acetylacetone mono(o-hydroxyanil) and related complexes[16] of copper(II) (**5** and **6**), and the binuclear structures attributed to these compounds on the basis of the magnetism were confirmed by X-ray structural determinations.[16–18] Structure **1** assigned to the present complexes resembles **5** and **6** in that the copper atoms are bridged by oxygen atoms joined to aromatic rings. In the present complexes the complex ligands have two phenolic oxygens in the cis position and are forced to act as bidentates.



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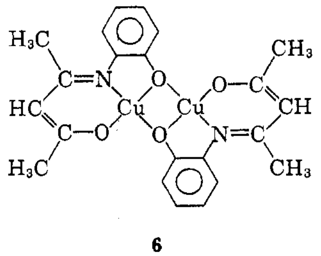

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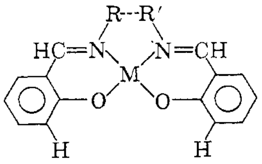
These complexes are unique in their bonding since one of the metals is "inside" the Schiff base and the other "outside" it, so that even for homonuclear complexes, the environments about the two metal atoms are necessarily different. The environment about each of the metal atoms can be varied by varying the Schiff bases and the other ligands.

While the well-established donor properties of Schiff base compounds,[5,6,8-10] together with the magnetic properties of the complexes $[(CuL)CuX_2] \cdot nH_2O$, leave no reasonable doubt about the binuclear structure of the latter types of complexes, the detailed stereochemistry about both the metal atoms is not quite so readily ascertained. The planar complexes CuES, Cu-1,2-PS, CuPS, CuMPS, CuEHA, and NiES presumably remain essentially planar when they act as ligands, but the second metal atom need not lie exactly in the same plane as the first metal and its four donor atoms. Moreover, the steric requirements of such a Schiff base ligand (**7**) closely resemble those of 2,2′-biquinolyl (**8**)



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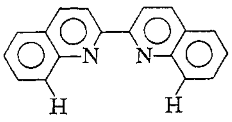

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which was used to obtain pseudo-tetrahedral complexes of copper(II),[19] as well as a five-coordinate gold(III) complex.[20] It is therefore likely that the metal atom outside the Schiff base will be in a tetrahedral or pseudo-tetrahedral environment. Certainly, the magnetic moments of cobalt(II) in the complexes $[(NiES)CoCl_2]$ and $[(CuES)CoCl_2]$ indicate that the cobalt atom is almost certainly in a tetrahedral rather than a planar environment,[21] though in the case of cobalt(II), a tetrahedral structure would be likely even in the absence of steric forcing. These moments are of the same order as the average value (4.8 BM) observed for the $CoCl_4^{2-}$ anion with a series of cations in the solid state.[22] However, magnetic moments generally found in octahedral cobalt(II) complexes are only a little higher ($\sim$5.2 BM) and, allowing for experimental error, the moment is a poor diagnostic for choosing between these two stereochemistries. Thus an infinite polymeric structure involving octahedral cobalt and chlorine bridges is not ruled out.[21] A similar polymeric structure is possible for the complex $[(CuPS)HgCl_2]$, although we consider this to be unlikely.

When the complex ligand CuL is planar, the copper coordinated to the halogen atoms in $[(CuL)CuX_2]$ is expected for steric reasons to be in a pseudo-tetrahedral environment.[19] Changes in the organic Schiff bases, L, can force a nonplanar configuration upon the complexes ML, as in going from L = ES to L = 1,3-PS. In this case, a trend toward increasing tetrahedral distortion as the diimine chain length is increased would be expected for the metal inside the Schiff base. We have communicated some of our results to our colleagues, who have observed in the zinc analogs of these complexes spectral changes attributable to such a trend.[23] Moreover, the electronic spectra of the anhydrous binuclear copper complexes $[(CuL)CuX_2]$ are best explained in terms of a pseudo-tetrahedral environment about at least one of the two copper atoms, with a greater degree of distortion in the bromo complex than in the analogous chloro derivative.[2] The complex $[(Cu\text{-}1,3\text{-}PS)CuCl_2]$ is the only one of the binuclear copper series in which the maximum in the χ_M *vs.* T curve is not observed within the experimental temperature range (Figure 1), and its fit to the Bleany–Bowers equation is not completely diagnostic for a binuclear structure. However, a Curie–Weiss dependence for the magnetism is poorer and requires $\theta = 111°K$. Although a polymeric structure involving chlorine bridges and octahedral structure for the copper atoms outside the Schiff base is not completely ruled out by the magnetism, the electronic spectrum[2] does not suggest octahedral coordination.

A further complication arises in the complexes containing a molecule of water, which could be coordinated to the metal atom inside the Schiff base, resulting in a square-pyramidal configuration about this metal, similar to the structure possessed by $(Cu\text{-}1,2\text{-}PS) \cdot H_2O$.[24] Thus, in some of the compounds, *e.g.*, $[(CuES)CuCl_2] \cdot H_2O$, which would otherwise have been expected to contain one planar metal atom, there may be one pseudo-tetrahedral and one square-pyramidal metal atom. Alternatively, it is not impossible that the water molecule is coordinated to the other metal atom, or trapped uncoordinated in the crystal lattice.

The stereochemistry about the metal atoms should influence the degree of orbital contribution to the magnetic moment and hence the estimated value of g, the lowest g value being expected if the environment about the metal atoms is planar. However, in binuclear copper(II) complexes, no significant trend is found in proceeding, for example, from complex **6** (g = 2.09) to copper(II) alkanoates. Thus, it would be unreasonable to attempt to correlate the experimental g values with those that might be expected from the postulated stereochemistries, *e.g.*, one planar and one pseudo-tetrahedral copper atom. In fact, it can be seen from Table IV that there is no correlation, within experimental error, between g values and likely stereochemistries in the present binuclear complexes. The complexes $[(CuEHA)CuCl_2]$ and $[(CuPS)CuBr_2] \cdot {}^1/_2H_2O$ have g values somewhat higher than the others in Table IV, but as the magnetic moments of these two compounds are rather low, errors in the measurements are higher than in the other complexes. The magnetic

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properties of both the complexes conform well to eq 2, so that they are likely to be binuclear like the other compounds.

The strength of the antiferromagnetic interaction, or the magnitude of J, is undoubtedly affected by many factors. Our influence which is likely to be of importance is the stereochemistry about the oxygen bridges. The relevance of this factor can be established by an extension of the study to a wider range of the present type of binuclear compounds, which allows great scope for variation of the stereochemistry.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Complexes of Trivalent Phosphorus Derivatives. III. Metal Carbonyl Complexes of 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene[1,2]

BY R. B. KING[3] AND K. H. PANNELL[4]

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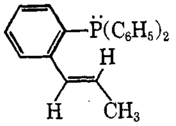
The reactions of various metal carbonyl derivatives with the novel unsaturated tertiary phosphine 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene ($C_8H_8PC_6H_5$) have been investigated. Cycloheptatrienetricarbonylmolybdenum reacts with $C_8H_8PC_6H_5$ at room temperature to give pale yellow *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_3$ where one of the two ligands is bonded to the metal atom through its phosphorus atom and one of its double bonds. In all other complexes of $C_8H_8PC_6H_5$ prepared in this work, only the phosphorus atom of this ligand is bonded to the metal atom. Hexacarbonylchromium reacts with $C_8H_8PC_6H_5$ to form a mixture of $(C_8H_8PC_6H_5)Cr(CO)_5$ and *trans*-$(C_8H_8PC_6H_5)_2Cr(CO)_4$. Hexacarbonylmolybdenum reacts with $C_8H_8PC_6H_5$ to give a mixture of $(C_8H_8PC_6H_5)Mo(CO)_5$ and *cis*-$(C_8H_8PC_6H_5)_2Mo(CO)_4$; however, the latter compound is better prepared from $C_8H_8PC_6H_5$ and cycloheptatrienetricarbonylmolybdenum at 100°. The monosubstituted yellow iron complex $(C_8H_8PC_6H_5)Fe(CO)_4$ may be prepared from $Fe(CO)_5$ and $C_8H_8PC_6H_5$ and the deeper yellow, relatively unstable, disubstituted iron complex *trans*-$(C_8H_8PC_6H_5)_2Fe(CO)_3$ from $Fe_2(CO)_9$ or $C_8H_8Fe(CO)_3$ and $C_8H_8PC_6H_5$. The mercury derivatives $Hg[Fe(CO)_3NO]_2$ and $Hg[Co(CO)_4]_2$ react with $C_8H_8PC_6H_5$ to form orange $Hg[Fe(CO)_2(NO)(C_8H_8PC_6H_5)]_2$ and yellow $Hg[Co(CO)_3(C_8H_8PC_6H_5)]_2$, respectively.

Introduction

Metal carbonyl derivatives of both tricovalent phosphorus compounds[5] and of olefins[6] have received much attention in recent years. However, metal carbonyl complexes of unsaturated phosphines have received much less attention. Interrante, Bennett, and Nyholm[7] have found (2-propenylphenyl)diphenylphosphine (I) to act as a bidentate ligand forming $[C_3H_5C_6H_4P(C_6H_5)_2]M(CO)_4$ (M = Cr, Mo, and W) compounds.

Recently Katz, Nicholson, and Reilly[8] have described the novel unsaturated phosphine 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, $C_8H_8PC_6H_5$ (II, abbreviated as "Ppb"), prepared from phenyldichlorophosphine and dipotassium cyclooctatetraenediide. This ligand is in theory capable of coordinating with a metal atom either as a tertiary phosphine, a monoolefin, or a conjugated diolefin depending on the bridge to which the metal atom is bonded. Furthermore, it is possible that two of the three bridges could coordinate simultaneously to the metal atom resulting in complexes in which the $C_8H_8PC_6H_5$ ligand is bonded to the metal atom either through the diolefin and olefin bridges, through the diolefin and tertiary phosphine bridges, or through the olefin and tertiary phosphine bridges. This paper reports the reactions of $C_8H_8PC_6H_5$ (II) with various metal carbonyl derivatives, especially those where more than one carbonyl group often are replaced with ligands.



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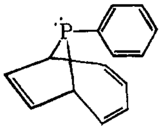

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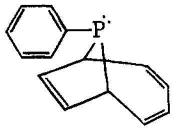

II′

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table II) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 421 or 621 spectrometer. In addition the spectra of the soluble compounds were investigated in the

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[4] Postdoctoral Research Associate supported by Grant AF-AFOSR-1211-67 from the Air Force Office of Scientific Research during the period Nov 1966–May 1967.

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