

triphenylphosphine, so the presence of the positive phosphetanium group three carbon atoms away does not appreciably influence the coordination properties of the diphenylphosphino group.

Acknowledgment.—The authors are grateful to Dr. T. D. DuBois for helpful discussions and to the National Science Foundation for financial support of this research (Grants GP-5729 and GP-8365).

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF NEW SOUTH WALES KENSINGTON, NEW SOUTH WALES 2033, AUSTRALIA,
AND THE DEPARTMENT OF PHYSICAL CHEMISTRY, VICTORIA UNIVERSITY, WELLINGTON, NEW ZEALAND

Metal Complexes as Ligands. VIII.¹ Square-Planar Binuclear Copper(II) Complexes with Ring-Substituted Salicylaldimines

By R. B. COLES, C. M. HARRIS, AND E. SINN

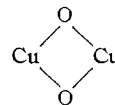
Received March 24, 1969

A series of copper(II) complexes with ring-substituted, bidentate salicylaldimine ligands and the corresponding binuclear copper halide derivatives has been prepared and studied. The spectral and magnetic properties of the parent mononuclear complexes and of their binuclear derivatives are interpreted in terms of an essentially planar environment about the copper atoms. No significant dependence of the stereochemistry upon the bulkiness of the substituent on the nitrogen atom of the salicylaldimine group is observed. These results contrast with those for the analogous complexes with no ring substituents, in which there is a strong dependence of the stereochemistry on the bulkiness of the nitrogen substituent in the parent mononuclear complexes and a similar but smaller dependence in the binuclear derivatives. The role of magnetic and infrared data as an analytical tool for the binuclear complexes is discussed.

Introduction

Many metal complexes with bi-, tri-, or tetradentate salicylaldimines react with other metal salts such as halides, nitrates, or perchlorates, to form various bi- and trinuclear complexes containing similar and dissimilar metals.¹⁻⁵ When both metal atoms in a binuclear complex or all three metals in a trinuclear complex are paramagnetic, antiferromagnetic interactions are usually observed.¹⁻⁷ In particular, when the copper(II) complexes of bidentate salicylaldimines (1, R' = H) are treated with copper(II) chloride,^{5,8} bromide,¹ or nitrate,⁹ binuclear complexes are formed (2, R' = H, X = Cl, Br, or ONO₂), with a *trans* arrangement of the

ligands about the

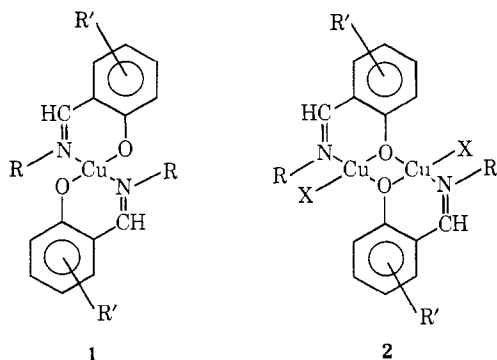


skeleton; these complexes exhibit pairwise antiferromagnetic interactions in all cases investigated.^{5,7} A strong trend from planar toward tetrahedral configuration as the nitrogen substituent R becomes more bulky has been observed in the parent complexes 1, R' = H,^{10,11} while a similar but much lesser trend was found in the binuclear complexes 2, R' = H.^{5,7,8}

We now report on the reaction of copper(II) halides with ring-substituted salicylaldimine complexes 1 (R' = 5-Cl, 5-Br, 3,5-(Cl)₂, 5-NO₂, 5,6-benzo) and compare the properties of the binuclear complexes formed with their analogs having no substituents (R' = H) in the phenyl rings of the salicylaldimine group.

Experimental Section

The organic ligands and their copper(II) complexes (1) were prepared by standard methods described in the literature¹²⁻¹⁷ using the appropriate primary amines and 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-



(1) Part VII: C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, **3**, 81 (1969).

(2) S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Letters*, **3**, 495 (1967).

(3) S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, **7**, 268 (1968).

(4) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

(5) C. M. Harris and E. Sinn, *ibid.*, **30**, 2723 (1968).

(6) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).

(7) S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Letters*, **4**, 107 (1968).

(8) G. E. Batley and D. P. Graddon, *Australian J. Chem.*, **21**, 1473 (1968).

(9) R. B. Coles, Thesis, University of New South Wales, 1968.

(10) L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, **4**, 407 (1965).

(11) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

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

(13) P. Pfeiffer and H. Krebs, *J. Prakt. Chem.*, **153**, 265 (1930).

(14) P. Pfeiffer and H. Krebs, *ibid.*, **155**, 77 (1940).

(15) L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).

(16) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(17) (a) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961); (b) P. Pfeiffer, E. Buchholz, and O. Bauer, *J. Prakt. Chem.*, **129**, 163 (1931).

TABLE I
 ANALYTICAL DATA FOR PARENT SALICYLALDIMINE COMPLEXES (SEE STRUCTURE 1)

R	R'	Molecular formula	Analyses, %					
			Calcd			Found		
			C	H	N	C	H	N
CH ₃	5,6-Benzo	C ₂₄ H ₂₀ N ₂ O ₂ Cu	66.7	4.8	6.5	67.0	4.7	6.0
C ₂ H ₅	5,6-Benzo	C ₂₈ H ₂₄ N ₂ O ₂ Cu	67.9	5.3	6.1	67.9	5.3	5.5
CH(CH ₃) ₂	5,6-Benzo	C ₂₈ H ₂₈ N ₂ O ₂ Cu	68.8	5.8	5.7	69.0	5.8	6.1
Cyclohexyl	5,6-Benzo	C ₃₄ H ₃₆ N ₂ O ₂ Cu	71.9	6.4	4.9	71.8	6.1	4.7
CH ₂ C ₆ H ₅	5,6-Benzo	C ₃₆ H ₂₈ N ₂ O ₂ Cu	74.0	4.8	4.8	73.9	4.8	4.5
CH ₃	5-Cl	C ₁₆ H ₁₄ N ₂ O ₂ Cl ₂ Cu	47.8	3.5	7.0	47.4	3.5	6.8
C ₂ H ₅	5-Cl	C ₁₈ H ₁₈ N ₂ O ₂ Cl ₂ Cu	50.3	4.2	...	50.3	4.0	...
(CH ₂) ₂ CH ₃	5-Cl	C ₂₀ H ₂₂ N ₂ O ₂ Cl ₂ Cu	52.4	4.9	...	52.4	4.9	...
CH(CH ₃) ₂	5-Cl	C ₂₀ H ₂₂ N ₂ O ₂ Cl ₂ Cu	52.4	4.9	...	52.1	4.8	...
Cyclopentyl	5-Cl	C ₂₄ H ₂₆ N ₂ O ₂ Cl ₂ Cu	56.5	5.2	...	56.5	5.4	...
Cyclohexyl	5-Cl	C ₂₆ H ₃₀ N ₂ O ₂ Cl ₂ Cu	58.1	5.6	...	57.9	5.8	...
CH ₃	5-Br	C ₁₆ H ₁₄ N ₂ O ₂ Br ₂ Cu	39.3	2.9	5.7	39.3	3.1	5.4
C ₂ H ₅	5-Br	C ₁₈ H ₁₈ N ₂ O ₂ Br ₂ Cu	41.8	3.5	...	41.5	3.5	...
(CH ₂) ₂ CH ₃	5-Br	C ₂₀ H ₂₂ N ₂ O ₂ Br ₂ Cu	44.0	4.1	...	44.0	3.9	...
CH(CH ₃) ₂	5-Br	C ₂₀ H ₂₂ N ₂ O ₂ Br ₂ Cu	44.0	4.1	5.1	43.7	4.0	5.1
Cyclopentyl	5-Br	C ₂₄ H ₂₆ N ₂ O ₂ Br ₂ Cu	48.2	4.4	...	48.0	4.5	...
Cyclohexyl	5-Br	C ₂₆ H ₃₀ N ₂ O ₂ Br ₂ Cu	49.9	4.8	4.5	49.7	5.0	4.3

nitrosalicylaldehyde, and 5,6-benzosalicylaldehyde. Some analytical data for these complexes are given in Table I.

The infrared and magnetic results are much better criteria than elemental analyses for the formation and purity of the binuclear complexes 2; this will be discussed further below. However some routine microanalyses were performed as a check and these are listed with the individual preparations.

Chloro(N-methyl-5,6-benzosalicylaldimino)copper(II).—Bis(N-methyl-5,6-benzosalicylaldimino)copper(II) (5 g) was dissolved in chloroform (300 ml) and copper(II) chloride dihydrate (1.5 g) in ethanol (25 ml) was added. The mixture was refluxed for 15 min and allowed to cool. On standing for 3 days a dark brown powder separated. *Anal.* Calcd for C₂₄H₂₀N₂O₂Cl₂Cu: C, 50.9; H, 3.5; N, 4.9; Cl, 12.5. Found: C, 51.0; H, 3.5; N, 4.8; Cl, 12.4.

Chloro(N-ethyl-5,6-benzosalicylaldimino)copper(II).—Bis(N-ethyl-5,6-benzosalicylaldimino)copper(II) (5 g) was refluxed in ethanol (200 ml) containing copper(II) chloride dihydrate (1.5 g) until all of the solid dissolved and the solution was a uniform red-brown color. After cooling, the solution was filtered and reduced to 50 ml. On standing for 14 days, fine red-brown crystals formed and were filtered off. *Anal.* Calcd for C₂₆H₂₄N₂O₂Cl₂Cu₂: C, 52.5; H, 4.1; N, 4.7. Found: C, 52.2; H, 4.1; N, 4.4.

Chloro(N-isopropyl-5,6-benzosalicylaldimino)copper(II) Monohydrate.—This compound was prepared by the same method as its methyl analog. A black-brown crystalline product resulted. *Anal.* Calcd for C₂₈H₃₀N₂O₂Cl₂Cu₂: C, 52.5; H, 4.7; N, 4.3. Found: C, 52.3; H, 4.6; N, 4.2.

Chloro(N-cyclohexyl-5,6-benzosalicylaldimino)copper(II).—Bis(N-cyclohexyl-5,6-benzosalicylaldimino)copper(II) (5 g) was dissolved in chloroform (1000 ml) and ethanol (200 ml). Copper(II) chloride dihydrate (1.5 g) in ethanol (25 ml) was added with stirring. On standing for 7 days, large black-brown crystals of the product were obtained. *Anal.* Calcd for C₃₄H₃₆N₂O₂Cl₂Cu₂: C, 58.5; H, 5.2; N, 4.0. Found: C, 58.7; H, 5.3; N, 3.7.

Chloro(N-methyl-5-chlorosalicylaldimino)copper(II) Monohydrate.—Bis(N-methyl-5-chlorosalicylaldimino)copper(II) (5 g) in chloroform (150 ml) and copper(II) chloride dihydrate (1.5 g) in ethanol (25 ml) were mixed. On refluxing, the light green parent complex dissolved, and an orange precipitate formed. This was filtered off after cooling. *Anal.* Calcd for C₁₆H₁₆N₂O₂Cl₄Cu₂: C, 34.8; H, 2.9; N, 5.1. Found: C, 34.9; H, 2.6; N, 4.8.

Chloro(N-ethyl-5-chlorosalicylaldimino)copper(II).—Bis(N-ethyl-5-chlorosalicylaldimino)copper(II) (5 g) was dissolved in hot chloroform (150 ml), and copper(II) chloride dihydrate (1.5 g) in ethanol (25 ml) was added. The mixture was refluxed for 1 hr,

and after cooling the green-black crystalline product was filtered off. *Anal.* Calcd for C₁₈H₁₈N₂O₂Cl₄Cu₂: C, 38.4; H, 3.2; N, 5.0. Found: C, 38.3; H, 3.5; N, 4.9.

Chloro(N-n-propyl-5-chlorosalicylaldimino)copper(II).—Prepared analogously to the above compound. A fine red-brown crystalline product resulted. *Anal.* Calcd for C₂₀H₂₂N₂O₂Cl₄Cu₂: C, 40.6; H, 3.8; N, 4.7. Found: C, 40.3; H, 3.8; N, 4.5.

Chloro(N-isopropyl-5-chlorosalicylaldimino)copper(II).—The black crystalline complex was prepared analogously to the above compound. *Anal.* Calcd for C₂₀H₂₂N₂O₂Cl₄Cu₂: C, 40.6; H, 3.8; N, 4.7. Found: C, 40.7; H, 3.6; N, 4.4.

Chloro(N-cyclopentyl-5-chlorosalicylaldimino)copper(II).—The deep red complex was prepared analogously to the above compound. *Anal.* Calcd for C₂₄H₂₆N₂O₂Cl₄Cu₂: C, 44.8; H, 4.1; N, 4.4. Found: C, 44.8; H, 4.1; N, 4.1.

Chloro(N-cyclohexyl-5-chlorosalicylaldimino)copper(II).—This was prepared analogously to the above complex yielding a red-brown powder. *Anal.* Calcd for C₂₆H₃₀N₂O₂Cl₄Cu₂: C, 46.5; H, 4.6; N, 4.2. Found: C, 46.2; H, 4.7; N, 3.8.

Chloro(N-methyl-5-bromosalicylaldimino)copper(II).—Bis(N-methyl-5-bromosalicylaldimino)copper(II) (5 g) was suspended in hot chloroform and copper(II) chloride dihydrate (1.5 g) in ethanol (25 ml) was added. A buff precipitate formed immediately. The mixture was refluxed until all of the light green starting material had dissolved, and the precipitate was filtered off on cooling. *Anal.* Calcd for C₁₆H₁₄N₂O₂Cl₂Br₂Cu₂: C, 30.8; H, 2.3; N, 4.5. Found: C, 30.5; H, 2.4; N, 4.0.

Chloro(N-ethyl-5-bromosalicylaldimino)copper(II).—The black-brown crystalline product was prepared by a method analogous to that used for chloro(N-ethyl-5-chlorosalicylaldimino)copper(II). *Anal.* Calcd for C₁₈H₁₈N₂O₂Cl₂Br₂Cu₂: C, 33.1; H, 2.8; N, 4.3. Found: C, 32.9; H, 2.8; N, 4.0.

Chloro(N-n-propyl-5-bromosalicylaldimino)copper(II).—The dark red-brown complex was prepared analogously to the above compound. *Anal.* Calcd for C₂₀H₂₂N₂O₂Cl₂Br₂Cu₂: C, 35.3; H, 3.3; N, 4.1. Found: C, 35.6; H, 3.4; N, 3.9.

Chloro(N-isopropyl-5-bromosalicylaldimino)copper(II).—The dark brown complex was prepared analogously to the above compound. *Anal.* Calcd for C₂₀H₂₂N₂O₂Cl₂Br₂Cu₂: C, 35.3; H, 3.3; N, 4.1. Found: C, 35.5; H, 3.4; N, 4.2.

Chloro(N-cyclopentyl-5-bromosalicylaldimino)copper(II).—The fine, dark brown, crystalline complex was prepared by a method analogous to that used for the above compound. *Anal.* Calcd for C₂₄H₂₆N₂O₂Cl₂Br₂Cu₂: C, 39.3; H, 3.6; N, 3.8. Found: C, 39.4; H, 3.7; N, 3.6.

Chloro(N-cyclohexyl-5-bromosalicylaldimino)copper(II).—This complex was obtained as a brown powder by a method analogous

TABLE II
 ANALYTICAL DATA FOR BINUCLEAR COMPLEXES WITH X = Br (SEE STRUCTURE 2)

R	R'	Molecular formula	Analyses, %							
			Calcd				Found			
			C	H	N	Br	C	H	N	Br
CH ₃	5,6-Benzo	C ₂₄ H ₂₀ N ₂ O ₂ Br ₂ Cu ₂	44.0	3.1	4.3	24.3	49.3	3.2	4.1	24.6
CH(CH ₃) ₂	5,6-Benzo	C ₂₈ H ₂₈ N ₂ O ₂ Br ₂ Cu ₂	47.3	4.0	3.9		47.6	4.1	4.1	
Cyclohexyl	5,6-Benzo	C ₃₄ H ₃₀ N ₂ O ₂ Br ₂ Cu ₂	51.6	4.6	3.5		51.7	4.7	3.4	
CH ₃	5-Cl	C ₁₆ H ₁₄ N ₂ O ₂ Cl ₂ Br ₂ Cu ₂	30.8	2.3	4.5		30.5	2.5	3.9	
CH ₃	5-Br	C ₁₆ H ₁₄ N ₂ O ₂ Br ₄ Cu ₂	26.9	2.0	3.9		26.6	2.2	3.5	

to the above. *Anal.* Calcd for C₂₆H₃₀N₂O₂Cl₂Br₂Cu₂: C, 41.0; H, 4.0; N, 3.7. Found: C, 41.0; H, 3.5; N, 3.5.

The copper bromide adducts (2, X = Br) of the various copper salicylaldimine complexes (1) were prepared by methods analogous to those used for the corresponding copper chloride adducts (using CuBr₂ in place of CuCl₂·2H₂O). Analytical data for these complexes are given in Table II.

Magnetic Measurements.¹⁸—Magnetic susceptibilities, χ_M , were determined by the Gouy method³ and diamagnetic corrections were estimated from Pascal's constants. For the antiferromagnetic complexes, and for them only, the magnetic moments μ_{eff} (Table III) were corrected for $N\alpha$, using eq 1, where T is the

$$\mu_{\text{eff}} = \sqrt{8T(\chi_M - N\alpha)} \quad (1)$$

absolute temperature, χ_M the magnetic susceptibility per gram-ion, and $N\alpha$, the temperature-independent contribution arising from the second-order Zeeman splitting, is given its usual value of 6×10^{-5} cgsu.

 TABLE III
 MAGNETIC MOMENTS, μ_{eff} (BM) OF COMPLEXES 1 AND MELTING POINTS (°C) OF 1 AND 2

Substituents ^a		Complex ^a			
R	R'	1	2, X = Cl	2, X = Br	
		μ_{eff}	Mp	Mp	Mp
CH ₃	5,6-Benzo	1.81	230	210	195
C ₂ H ₅	5,6-Benzo	1.82	230		
(CH ₂) ₂ CH ₃	5,6-Benzo		189		
CH(CH ₃) ₂	5,6-Benzo	1.80	191	185	174
Cyclopentyl	5,6-Benzo	1.82	200		
Cyclohexyl	5,6-Benzo	1.85	203	208	190
CH ₃	5-Cl	1.83	236	238	200
C ₂ H ₅	5-Cl	1.86	207	214	
(CH ₂) ₂ CH ₃	5-Cl	1.84	159	206	
CH(CH ₃) ₂	5-Cl	1.83	170	200	
Cyclopentyl	5-Cl	1.84	158	207	
Cyclohexyl	5-Cl	1.81	202	221	
CH ₃	5-Br	1.82	242	240 ^b	212
C ₂ H ₅	5-Br	1.80	225	193	
(CH ₂) ₂ CH ₃	5-Br		181	208	
CH(CH ₃) ₂	5-Br		164	206	
Cyclopentyl	5-Br		176	213	

^a See structures 1 and 2. ^b Decomposes.

Electronic Spectra.—Visible, ultraviolet, and near-infrared spectra were determined by reflectance on the solid compounds using a Carl Zeiss Type M4Q111 spectrophotometer.

Infrared measurements were made as described previously,⁴ using a Perkin-Elmer SP200 and a Hitachi 521 spectrometer.

Results and Discussion

Infrared and Magnetic Data as Analytical Criteria.—Extensive elemental analyses were made for binuclear

(18) The detailed magnetic susceptibility data have been deposited as Document No. NAPS-00546 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

complexes analogous to the present series with no substituents (2, R' = H),^{1,5,7} but infrared and magnetic susceptibility data were found to be better criteria for the formation and purity of the binuclear complexes. Significant differences are observed in the infrared spectrum of the parent Schiff base complex (the "complex ligand") before and after the formation of bi- or trinuclear derivatives, including a shift to higher energy (15–20 cm⁻¹) in the band near 1530 cm⁻¹, smaller shifts in the bands near 1620, 1480, 1140, and 760 cm⁻¹, and the appearance of new bands near 1275, 1210, and 1150 cm⁻¹. Such changes in the infrared spectrum are completely characteristic of the formation of the bi- and trinuclear complexes^{1,4,5,7} and were therefore able to be used as simple and immediate criteria for the formation of the desired binuclear complexes of the present series. In the 5,6-benzo-substituted complexes alone, there are several absorptions near 1530 cm⁻¹, and the desired band is difficult to identify, but the other changes in the infrared spectrum still serve as criteria for binuclear complex formation. Table IV gives some relevant infrared band positions for typical complexes of types 1 and 2.

 TABLE IV
 INFRARED PEAKS NEAR 1620, 1530, AND 1250 CM⁻¹ IN THE RING-SUBSTITUTED COPPER SALICYLALDIMINES 1 AND THEIR COPPER HALIDE ADDUCTS 2

Substituents ^a		Complex ^a		
R	R'	1	2, X = Cl	2, X = Br
CH ₃	5-Cl	1624 s	1630 s	1630 s
		1532 m	1548 m	1548 m
			1270 s	1272 s
C ₂ H ₅	5-Br	1240 m	1247 s	1245 s
		1633 s	1649 s	1642 s
		1533 m	1550 m	1552 m
		1283 s	1273 s	
		1235 w	1235 vw	1252 s

^a See structures 1 and 2. Abbreviations for intensities: s, strong; m, medium; w, weak; vw, very weak.

Like the previously described^{1,5} binuclear complexes of type 2 with R' = H, the present series of ring-substituted complexes all exhibit antiferromagnetic interactions, and their magnetic properties can be represented by the Bleaney-Bowers equation¹⁹

$$\chi_M = \frac{g^2 \beta^2 N}{kT} (3 + e^{-2J/kT})^{-1} + N\alpha \quad (2)$$

(19) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London)*, **A214**, 451 (1952).

where β is the Bohr magneton, N Avogadro's constant, k the Boltzmann constant, g the Landé splitting factor, and J the exchange integral which gives a measure of the strength of the interaction. The values of J and g for best fit of the results to eq 2 are given in Table V and some of the results are plotted in Figure 1. As expected, the compounds tend toward diamagnetism at low temperatures, whereas paramagnetism normally increases markedly with decreasing temperature. Because of the method of preparation, the only impurities likely to be present in significant quantities are the parent complexes 1 or possibly the copper salt CuX_2 used. Such impurities will behave as simple paramagnets and form a source of strongly increasing magnetic susceptibility at low and decreasing temperatures; at these temperatures the contribution of the pure binuclear complex is relatively small and of known magnitude from the fit of data at higher temperatures to eq 2. In this way quantities of impurities too small to affect the elemental analyses are readily detected. As no conceivable impurities could reproduce the Bleaney-Bowers behavior of the pure binuclears, this is a highly specific test for purity. (It is possible that small deviations from the Bleaney-Bowers equation will result from anomalous behavior intrinsic to the compound in some cases, and therefore such deviations need not give a good measure of the quantity of paramagnetic impurities present, although agreement with the equation still indicates the absence of appreciable amounts of paramagnetic impurities and other anom-

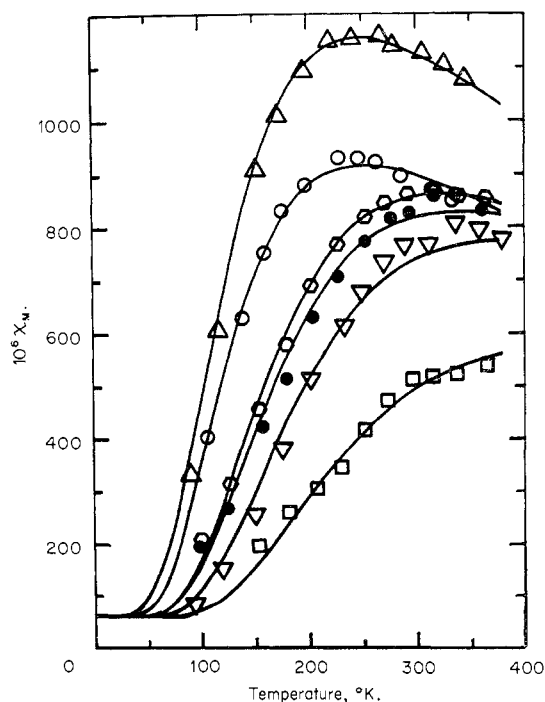


Figure 1.—Magnetic susceptibilities χ_M at various temperatures for the complexes 2: Δ , R = $\text{CH}(\text{CH}_3)_2$, R' = 5-Cl, X = Cl; \circ , R = C_2H_5 , R' = 5-Cl, X = Cl; \circ , R = CH_3 , R' = 5-Br, X = Br; \bullet , R = $(\text{CH}_2)_2\text{CH}_3$, R' = 5-Cl, X = Cl; ∇ , R = cyclopentyl, R' = 5-Br, X = Cl; \square , R = cyclohexyl, R' = 5,6-benzo, X = Cl. The curves are calculated from eq 2 using the values of J and g listed in Table V.

alous behavior.) The magnetic data (Figure 1) indicate that purity is satisfactory by this criterion and that the complexes with R' = 5,6-benzo generally contain a greater proportion of paramagnetic impurities than the others. Similar use of magnetic measurements in an analytical capacity has been made in analogous situations for various metals.²⁰⁻²³

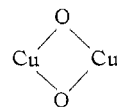
TABLE V
VALUES OF J (CM^{-1}) AND g FOR COMPLEXES 2

Substituents ^a	R	X	Ring substituents in R' ^a					
			5,6-Benzo		5-Cl		5-Br	
			J	g	J	g	J	g
CH_3		Cl	-173	2.14	-280	2.15	-220	2.23
C_2H_5		Cl			-140	2.14	-200	2.30
$(\text{CH}_2)_2\text{CH}_3$		Cl			-188	2.35	-180	2.26
$\text{CH}(\text{CH}_3)_2$		Cl	-97	2.30	-136	2.38	-195	2.22
Cyclopentyl		Cl	-160	2.20	-132	2.28	-210	2.38
Cyclohexyl		Cl	-130	2.10	-250	2.20	-215	2.32
CH_3		Br	-175	2.20	-146	2.20	-140	2.35
$\text{CH}(\text{CH}_3)_2$		Br	-135	2.22				
Cyclohexyl		Br	-114	2.16				

^a See structure 2.

Epr studies were carried out on four of the binuclear compounds 2 at room temperature and at 77°K, and no signals due to paramagnetic impurities were observed.

Magnetism and Stereochemistry.—The values of J and g (Table V) for the various complexes 2 appear to be randomly distributed showing no systematic trend with R, R', or X. Thus the magnitudes of J and g must be determined essentially by lattice effects. Apparently there is one basic



skeleton for all of the complexes, and this is very little affected by the other parts of the molecule except insofar as they affect the lattice. The magnetic moments (Table III) of the parent complexes 1 fall into a very small range about 1.83 BM, indicating that the stereochemistry about the copper atom is not noticeably influenced by the substituent groups R, R', and X. This contrasts with the increase in the moments observed in the analogs of 1 without ring substituents (R' = H), as R' becomes more bulky, a trend interpreted in terms of steric distortion from planar toward tetrahedral stereochemistry.^{5,11} Thus it appears that in the ring-substituted complexes 1 and 2, the copper atoms are essentially planar and the steric crowding of the R groups on the nitrogens is relieved mainly by distortion of the organic part of the molecules. This argument is supported by structural determinations on other sterically crowded copper(II) complexes: although steric effects lead to distortion from planar

(20) A. P. Ginsberg, E. Koubek, and H. J. Williams, *Inorg. Chem.*, **5**, 1656 (1966).

(21) C. M. Harris and E. Sinn, *Inorg. Chim. Acta*, **2**, 296 (1968).

(22) E. Sinn, *ibid.*, **3**, 11 (1969).

(23) K. E. Hyde, G. Gordon, and G. F. Kokoszka, *J. Inorg. Nucl. Chem.*, **30**, 2155 (1968).

TABLE VI
LIGAND FIELD SPECTRA (CM⁻¹) OF RING-SUBSTITUTED COPPER SALICYLALDIMINES
1 AND THEIR COPPER HALIDE ADDUCTS 2

Substituents ^a		Complex ^a					
R	R'	1		2, X = Cl		2, X = Br	
CH ₃	5,6-Benzo		14,600		11,200	15,800	14,300
C ₂ H ₅	5,6-Benzo	15,800	14,100				
(CH ₂) ₂ CH ₃	5,6-Benzo	15,600					
CH(CH ₃) ₂	5,6-Benzo	16,000	12,700	14,000	11,600	16,400	
Cyclohexyl	5,6-Benzo	15,700	13,800	14,700	10,300	16,100	
CH ₃	5-Cl	17,200	14,600		9,500	15,500	12,600
C ₂ H ₅	5-Cl	15,800	14,100	15,700	12,500		
(CH ₂) ₂ CH ₃	5-Cl	15,600		15,800	12,900		
CH(CH ₃) ₂	5-Cl	18,000	14,700	14,800	12,200		
Cyclopentyl	5-Cl	18,200	14,000	15,000			
Cyclohexyl	5-Cl	17,700	(15,000)	16,200	12,600		
CH ₃	5-Br	16,200			11,800	15,300	12,300
C ₂ H ₅	5-Br	15,800	13,800	15,700	12,600	15,700	13,500
(CH ₂) ₂ CH ₃	5-Br	15,800	14,300	15,700	12,700		
CH(CH ₃) ₂	5-Br	18,100	15,000	15,000	12,100		
Cyclopentyl	5-Br	17,300	12,400	14,800			
Cyclohexyl	5-Br	17,500	15,300	16,000	12,600		

^a See structures 1 and 2.

toward tetrahedral stereochemistry about the metal atom, the degree of distortion is generally much less than would be expected purely from steric considerations; instead, the ligands themselves undergo considerable distortion.²⁴⁻²⁶ Sacconi and Ciampolini¹¹ have already suggested that at least one of the complexes of type 1 (R' = 5-Cl, R = CH(CH₃)₂) is planar.

A comparison between the complexes 1 of bidentate salicylaldimines and their nickel(II) analogs shows that the effect of R and R' upon the stereochemistries about the copper and nickel is remarkably similar for the two metals. In the unsubstituted salicylaldimines (R' = H), both copper(II) and nickel(II) are fairly close to planar when R is an *n*-alkyl group, but both are considerably distorted toward tetrahedral when R is a *sec*-alkyl or *t*-butyl group. However, for the ring-substituted nickel(II) salicylaldimines, where R' = methyl, isopropyl, or phenyl,²⁷ or a chloro group,²⁸ the nickel atom was found to be planar for all R groups except *t*-butyl. The electronic spectra of complexes 1 and 2 lend further support to these observations.

Electronic Spectra.—Table VI gives the electronic spectra of the "complex ligands" 1 and their binuclear derivatives 2 in the region 8000–18,000 cm⁻¹. The spectra in this region are expected to contain the ligand field transitions and to give some indication of the stereochemistry about the metal atom.^{1,4,5,7,11} It seems that complexes of types 1 and 2 have two ligand field bands in this region, but it was not possible to observe both of these bands in some cases (especially R = CH₃) because of the interference of intense charge-transfer bands near or above 20,000 cm⁻¹.

The most noteworthy feature of the spectra of the binuclear complexes 2 is the absence of any significant dependence of the band positions upon the bulkiness of the R group on the nitrogen. This indicates again that any steric strain set up by R is taken up largely by the organic part of the molecule, while the stereochemistry about the metal is not greatly affected. This is in contrast to the slight trend to lower energies of the ligand field bands of the unsubstituted (R' = H) complexes analogous to 2 with increasing bulkiness of R, due to slight distortion from planar toward tetrahedral stereochemistry.^{1,5,7,8}

In the unsubstituted (R' = H) copper(II) salicylaldimines 1 the well-documented^{24,29-32} trend from near-planar toward tetrahedral stereochemistry, as R becomes bulkier, is accompanied by a dramatic decrease in energy of the ligand field transitions.^{1,5,7,8,11} However, in the ring-substituted complexes 1, no such trend is observed (Table VI). If anything, the trend is in the wrong direction, although the fluctuations appear to be largely random. These fluctuations are most likely due to various strengths of the weak copper-oxygen bonds which often form between neighboring molecules of planar copper complexes with ligands coordinated through oxygens. Such weak intermolecular copper-oxygen bonds have been demonstrated in copper(II) salicylaldimines.^{32,33}

In general, the binuclear chloro complexes (2, X = Cl) have their ligand field transitions at lower energies than the parent complexes 1, and the binuclear bromo complexes have them at lower energies still (Table VI). This may be attributed to the changes in the ligand fields when the ligands are changed from those (1) having the donor atoms N, O, N, O to those having

(24) T. P. Cheeseman, D. Hall, and T. N. Waters, *Proc. Chem. Soc.*, 379 (1963).

(25) E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 252 (1967).

(26) T. P. Cheeseman, D. Hall, and T. N. Waters, *ibid.*, A, 685 (1966).

(27) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

(28) L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).

(29) E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Sheringer, and C. Freiburg, *Acta Cryst.*, **14**, 1222 (1961).

(30) L. Sacconi and I. Bertini, *Inorg. Chem.*, **5**, 1520 (1966).

(31) P. L. Orioli and L. Sacconi, *J. Am. Chem. Soc.*, **88**, 277 (1966).

(32) D. Hall, S. V. Sheat, and T. N. Waters, *Chem. Commun.*, 436 (1966).

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

N, O, O, Cl or N, O, O, Br. The absence of any significant dependence of the spectra of complexes 1 and 2 upon R indicates that the stereochemistries are also not very dependent on R. These results are best explained if the copper atoms are essentially planar, in agreement with the conclusions from the magnetic data.

Formation of the Complexes.—As expected from the ease of formation of complexes analogous to 2 without ring substituents,^{1,5,7} the copper halid eadducts of the copper(II) complexes of 5-chloro- and 5-bromosalicylaldehydes were formed readily by similar methods. The binuclear complexes derived from 5,6-benzosalicylaldehyde were much more difficult to prepare, and in some cases the reaction mixtures had to stand for up

to 2 weeks before sufficient yields of the complexes were obtained, and in other cases, *viz.*, when R = *n*-propyl, *n*-butyl, *n*-octyl, and cyclopentyl, only the starting materials were recovered. Of the *n*-alkyls, only the methyl complexes could be prepared in sufficient quantities for magnetic and spectral measurements. Binuclear complexes derived from copper(II) 5-nitrosalicylaldehydes and 3,5-dichlorosalicylaldehydes also failed to form, probably because of the low solubility of the starting materials.

Acknowledgments.—The authors are grateful for ARGC support of this work. Thanks are due to Dr. E. Challen for microanalyses and to Mr. M. Collins for access to epr facilities.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MASSACHUSETTS, AMHERST, MASSACHUSETTS 01002

Pentacoordinated Molecules. XIV.¹ Molecular Vibrations and Stereochemical Nonrigidity of the Trigonal-Bipyramidal Model MX_3Y_2

By ROBERT R. HOLMES, SR. ROSE MARY DEITERS, AND JAMES A. GOLEN

Received March 26, 1969

Based on complete infrared and Raman vibrational spectra, a normal mode analysis of the series of trigonal-bipyramidal molecules PF_5 , AsF_5 , VF_5 , PCl_3F_2 , PCl_5 , SbCl_5 , $\text{Sb}(\text{CH}_3)_5$, and NbCl_5 has led to a description of the ground-state motions. Barrier energies for intramolecular exchange are compared for a square-pyramidal and tetragonal-pyramidal intermediate. The conclusion shows that either process gives a similar ordering and magnitude of barrier energies for these molecules. Examination of appropriate combinations of bending coordinates modified in most cases by ligand reorganization leads to a classification of model processes for intramolecular exchange mechanisms in terms of relative strengths of equatorial and axial bonds. Application is seen in transition metal chemistry. Further, transferability of data allows estimation of an exchange barrier for the hypothetical PH_5 molecule. The latter is considered the only case where a tunneling mechanism for exchange might be significant.

Introduction

Vibrational data have now appeared on a sufficient number of trigonal-bipyramidal molecules of D_{3h} symmetry to warrant a systematic normal mode analysis. Such an analysis while defining an appropriate force field allows an estimate of the "rigidity" of this class of molecules with respect to stereochemical change.

A particularly interesting change to a tetragonal-pyramidal structure has been discussed² in connection with a plausible mechanism³ by which some trigonal bipyramids undergo intramolecular exchange as observed by nmr measurements.^{4,5} What is needed is some insight into other possible intramolecular processes and an examination of their relative importance.

By analyzing internal motions of a series of related molecules showing variations in both ligands and central atoms, useful statements regarding competitive mechanisms should result.

For the molecules to be considered, infrared and Raman spectra have been recorded and fundamental frequency assignments have been made in each case. Most of the vibrational data are recently available and have been the subject of some force constant analyses.⁶⁻¹³

It is the purpose of this paper to attempt to identify the various types of stereochemical changes involved in intramolecular rearrangements of trigonal-bipyramidal molecules that may be induced by internal vibrational modes. Based on vibrational data and bonding

(1) Previous paper: R. R. Holmes and R. M. Deiters, *J. Chem. Phys.*, in press. Abstracted in part from Ph.D. dissertation of James A. Golen, University of Massachusetts, Amherst.

(2) R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, **7**, 2229 (1968).

(3) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(4) (a) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963); (c) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (d) R. R. Holmes and R. N. Storey, *ibid.*, **6**, 2146 (1966).

(5) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Am. Chem. Soc.*, **89**, 2017 (1967).

(6) H. Siebert, *Z. Anorg. Allgem. Chem.*, **265**, 303 (1951).

(7) P. C. Haarhoff and C. W. F. T. Pistorius, *Z. Naturforsch.*, **14a**, 972 (1959).

(8) P. C. Van Der Voorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, **43**, 3457 (1965).

(9) G. Nagarajan, *Indian J. Pure Appl. Phys.*, **2**, 278 (1964), and references cited therein.

(10) M. Radhakrishnan, *ibid.*, **1**, 437 (1963).

(11) R. A. Condrate and K. Nakamoto, *Bull. Chem. Soc. Japan*, **39**, 1108 (1966).

(12) H. H. Claassen and H. Selig, *J. Chem. Phys.*, **44**, 4039 (1966).

(13) L. C. Hoskins and R. C. Lord, *ibid.*, **46**, 2402 (1967).