sumed that the complex is an example of nickel(II) in a planar environment.

On the basis of evidence presented in earlier sections, it is concluded that the compounds CoX_2L_2 (X = Cl, Br, I, NCS) contain Co(II) in pseudotetrahedral environments and the compounds NiX_2L_2 (X = Cl, Br, I) for which two solid forms can be isolated (diamagnetic and paramagnetic) contain planar and tetrahedral Ni(II), respectively. Both solid modifications dissolve in CH_3NO_2 to give solutions containing predominantly tetrahedral nickel. Interconversion of modifications can be achieved easily. The planar isomers may be converted to tetrahedral by dissolution in a suitable solvent or in the solid phase by heating at 110°. The tetrahedral forms revert to planar upon standing for several weeks. The compound $Ni(NCS)_2 \cdot 2(morph)_3PO$ has been assigned a planar structure while it was not possible to make a definite assignment for $M(NO_3)_2 \cdot 2HMPA$ (M = Co(II), Ni(II)).

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Tridentate Schiff Base Complexes of Copper(II)[1,2]

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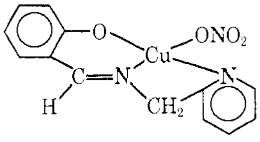
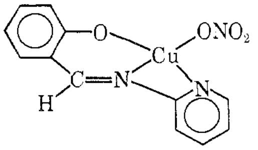
Tridentate Schiff base ligands yield complexes with copper(II) which frequently exhibit unusual properties. The low magnetic moment observed by Kishita, Muto, and Kubo[3] for acetylacetonemono(*o*-hydroxyanil)copper(II) stimulated extensive structural and magnetic investigations,[4-7] and these have led to a better understanding of the mechanisms of spin–spin coupling in magnetically condensed complexes. Unusual structures have also been obtained with these ligand systems. For example, pyridine-2-carboxaldoxime forms a trinuclear copper complex with a tridentate sulfate ion and four-coordinated oxygen.[8] In order to identify some of the factors which contribute to the donor properties of tridentate ligands, we have prepared and characterized a series of complexes with these ligands in which the donor atoms, the substituents on the donor atoms, and the donor atom linkages have been systematically varied. Here we report the results of our work with ligands having two nitrogen and one oxygen donor atoms.

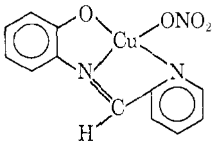
Experimental Section

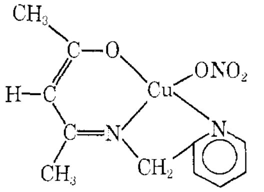
Preparation of the Complexes. N-(2-Dimethylaminoethyl)-salicylaldiminatocopper(II) Nitrate.—A series of complexes were prepared with substituted salicylaldehydes and N,N-dimethylethylenediamine. The appropriate salicylaldehyde (10 mmol) and N,N-dimethylethylenediamine (0.88 g, 10 mmol) were dissolved in 200 ml of isopropyl alcohol, and the resultant solution was heated at reflux for approximately 20 min. Copper nitrate trihydrate (1.20 g, 5 mmol) in 50 ml of anhydrous methyl alcohol and solid basic copper carbonate (0.55 g, 2.5 mmol) were added to the boiling solution, and the mixture was stirred vigorously while maintained at reflux for 30 min. The solution was filtered and reduced by evaporation to a volume of 150 ml. The dark green crystals which separated were collected on a Büchner funnel and washed with two 20-ml portions of isopropyl alcohol. The analytical data are given in Table I.

Schiff Bases Containing a Pyridine Ring.—Compounds VI–IX shown below in the most simple but not necessarily structurally correct formulations were prepared by the same general procedure described above. Ethyl alcohol was used as the solvent. The analytical data are given in Table II.


VI


VII


VIII


IX

Physical Measurements.—Magnetic susceptibilities were determined at room temperature and at 77°K using procedures described previously.[9] Infrared spectra of mulls and chloroform solutions were recorded on a Perkin-Elmer Model 137 spectrophotometer, visible spectra with a Cary Model 14 spectrophotometer, and conductivities of nitrobenzene solutions with a standard bridge. The experimental details and supporting data will be tabulated elsewhere.[10]

Results and Discussion

The most interesting result of this work obtains with compound VII. The infrared spectrum shows bands at 1020, 1310, and 1520 cm^{-1} which are due to coordinated nitrate,[11] and the conductivity of 3.12 ohm^{-1} in a 10^{-3} *M* nitrobenzene solution[12] confirms the infrared results. The magnetic moment at room temperature is 1.3 BM per copper ion, and this decreases to 1.0 BM

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[1] This is part X of the series "Spin–Spin Coupling in Magnetically Condensed Complexes."

[2] This research was supported by the National Science Foundation.

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[8] B. F. Hoskins, private communication.

[9] W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

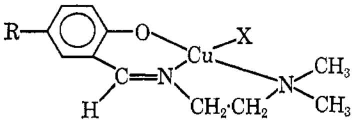
[10] F. L. Bunger, Ph.D. Thesis, University of North Carolina, Chapel Hill, N. C.

[11] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

[12] See, for example, F. Morris and R. S. Nyholm, *ibid.*, 4375 (1956).

TABLE I

ANALYTICAL DATA FOR



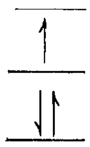
Compd no.	R	X	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
I	H	NO_3	41.70	41.90	4.77	4.56	13.26	13.21
II	Cl	NO_3	37.62	37.70	4.01	3.90	11.96	12.24
II	Br	NO_3	33.38	33.24	3.56	3.60	10.61	10.40
IV	NO_2	NO_3	37.45	37.35	4.28	4.02	14.86	14.82
V	H	Cl	45.52	45.50	5.21	5.45	9.65	9.76

TABLE II

ANALYTICAL DATA FOR COMPOUNDS VI–IX

Compd	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
VI·H_2O	45.25	45.30	3.40	3.60	12.15	11.85
VII·2.5H_2O	39.13	38.87	3.80	3.50	11.41	11.82
VIII·2H_2O	40.11	40.36	3.62	3.60	11.70	12.07
IX	41.97	42.13	4.16	4.19	13.35	13.11

at 77°K. The magnetic data are most easily explained on the basis of a trinuclear structure. Here $\mu_{\text{eff}} = \sqrt{{}^1/_3(0^2 + 0^2 + 1.73^2)} = 1.0$ BM. The doublet ground state arises from the spin–spin interaction of the three odd electrons to give the configuration

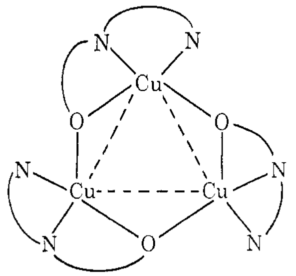


Since the doublet state is twofold degenerate and the quartet state lies at $-3J$,[13] then the temperature dependence of μ_{eff}^2 is

$$\mu_{\text{eff}}^2 = \frac{g^2}{3}\left(\frac{3 + 15\exp(-3J/kT)}{4 + 4\exp(-3J/kT)}\right)$$

where J is a negative number. We have not attempted to evaluate J, but the discernible temperature variation should permit this to be done once enough data are collected on similar compounds to assign with confidence values to g and TIP.

Structure X tentatively suggested for the compound is similar to that found for the trimeric pyridine-2-carboxaldoxime complex.[8] However, in this instance, one nitrate ion is probably bonded to each copper ion, either above or below the plane of the molecule, and the other coordination position on each copper may be occupied by a water molecule.



X

It is important to compare the results for compound VIII with trinuclear compound VII. Ligands in VII and VIII are structural isomers, yet compound VIII exhibits a normal magnetic moment (1.87 BM) and coordinated nitrate. Based on the magnetic data, the compound must be assigned a monomeric structure. It may be argued that VIII is also trinuclear but that the exchange coupling constant is very small and the magnetic data do not reflect the interaction. Studies at low temperatures will resolve the quandry.

The other compounds (I–IV) exhibited bands (both in solution and as mulls) in the infrared spectra at 1473–1480, 1280–1290, 1000–1020, and 810–837 cm^{-1} due to coordinated nitrate. It was possible to identify these bands by a comparison of the spectra of compounds I–IV with that of V which contained coordinated chloride. The low conductivities of 10^{-3} M solutions (0.2–9.0 ohm^{-1}) confirm that the nitrate ion is coordinated. Temperature-independent moments of 1.85–1.90 BM were observed.

The reflectance and solution spectra of compounds I–V are similar as expected. The charge-transfer band ($\epsilon_{\max} \approx 5000$) occurs near 390 m$\mu$ and the d–d band envelope ($\epsilon_{\max} \approx 200$) near 610 m$\mu$. For comparison we note that the visible absorption of bis(salicylaldehyde)-ethylenediiminatocopper(II) occurs at 545 mμ.[14] This shift to the red is a reflection of the poorer donor qualities of the tertiary amine nitrogen and nitrato oxygen atoms. The band intensities for the complexes falls between that of *trans*-centric bis(salicylaldiminato)copper(II) ($\epsilon_{\max}$ 123) and *cis*-acentric bis(salicylaldehyde)ethylenediiminatocopper(II) ($\epsilon_{\max}$ 396).[15]

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