length of Herschbach and Laurie[45] and their parameters for atoms in rows 1 and 5 of the periodic table, the difference in the lengths[46] of the two Au-C bonds can be estimated to be $d(\text{Au-C})_{\text{trans CH}_3} - d(\text{Au-C})_{\text{trans P}} = 0.03$ Å. The Au-C bond lengths also can be calculated using the Herschbach-Laurie parameters as a check on the internal consistency of the calculations. For the shorter Au-C bond of $(CH_3)_3AuP(CH_3)_3$ ($f = 2.42$ mdyn/Å), the value $d(\text{Au-C}) = 2.11$ Å is calculated, close to that used in the normal-coordinate analyses, 2.05 Å. Since the calculated values of the force constants are insensitive to small changes in bond length, essentially the same set of force constants would be obtained using 2.11 Å as input for the computation. The interaction constant $f(\text{Au-C,Au-P})_{\text{trans}}$ also has a negative value as in the case of $CH_3AuP(CH_3)_3$. In the case of the trimethylgold(III) compounds, a tertiary phosphine or arsine again is needed to stabilize the compound. The interaction constant $f(\text{Au-C,Au-C})_{\text{trans}}$ is positive. This indicates a shortening of the Au-C bond as the trans Au-C bond is lengthened, and all of the available experimental evidence indicates that the Au-C bonds are stronger in the dimethyl than in the trimethylgold compounds.

The trimethylarsine analog, $(CH_3)_3AuAs(CH_3)_3$, has very similar parameters for the trimethylgold moiety, although the force constant for Au-As stretching is considerably less than for Au-P bond stretching. The difference $f(\text{Au-C})_{\text{trans CH}_3} - f(\text{Au-C})_{\text{trans P}}$ is 0.24 mdyn/Å, corresponding to a difference of 0.03$_7$ Å in bond lengths.

The values of the force constants for Au-C stretching of the mutually trans bonds in $(CH_3)_3AuP(CH_3)_3$ and $(CH_3)_3AuAs(CH_3)_3$ and the single bond in $CH_3AuP(CH_3)_3$ all are the same within the experimental error 2.2$_5$, 2.3$_1$, and 2.3$_0$ mdyn/Å, respectively. This suggests that these bonds are nearly identical, and this correlates well with the similarity in the rates of electrophilic attack by $HgBr_2$ on them in the gold(I)- and gold(III)-phosphine complexes.[7]

Although comparisons of force constants for molecules of appreciably different structures is considerably less accurate than for related structures, it may be noted that the force constants for Au-C bond stretching of the mutually trans Au-C bonds are essentially the same as the value for Hg-C stretching, $f(\text{Hg-C}) = 2.3_3$ mdyn/Å, calculated[40] with data for both $(CH_3)_2Hg$ and $(CD_3)_2Hg$. The interaction constant $f(\text{HgC,HgC}) = 0.06$ mdyn/Å is of the same sign but smaller than the corresponding constants in the gold(III) complexes. Both Au-C force constants are smaller than the values for $[(CH_3)_2AuCl_2^-]$, $f(\text{Au-C}) = 2.8_1$ (06) mdyn/Å, or $[(CH_3)_2AuBr_2^-]$, $f(\text{Au-C}) = 2.7_2$ (09) mdyn/Å.[26]

The Au-P valence force constants are essentially the same for the organogold(I) and -gold(III) compounds. The Urey-Bradley Au-P constant is smaller with Au(III), since these square-planar complexes have two P· · ·C nonbonded constants which correlate highly with $K(\text{Au-P})$. This suggests that the small value used for $F(\text{P}\cdot\cdot\cdot\text{C})$, 0.075 mdyn/Å, is still too large.

Oxidative addition of RX to CH_3AuPR_3 should be energetically favorable in many instances, since the Au-PR_3 bond strength will be altered little. Since the Au-C bond of CH_3AuPR_3 is similar to the weaker trans bonds in $(CH_3)_2AuP(CH_3)_3$, the exchange reaction (eq 6) observed by Tamaki

$$(CH_3)_2AuXPR_3 + CH_3AuPR_3 \rightleftarrows (CH_3)_3AuPR_3 + XAuPR_3 \qquad (6)$$

and Kochi for X = I[8] would be expected to involve little enthalpy change.

Registry No. *cis*-$(CH_3)_2(CD_3)AuP(CH_3)_3$, 38386-64-0; $(CD_3)_3AuP(CH_3)_3$, 38386-65-1; $(CH_3)_3AuAs(CH_3)_3$, 38386-66-2; $CH_3AuP(CH_3)_3$, 32407-79-7; $CD_3AuP(CH_3)_3$, 38386-67-3; $(CH_3)_3AuP(CH_3)_3$, 33012-33-8; $ClAuP(CH_3)_3$, 15278-97-4; $BrAuP(CH_3)_3$, 25884-75-7; $IAuP(CH_3)_3$, 25892-35-7.

(45) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 35, 458 (1961).

(46) H. P. Fritz, W. P. Griffith, G. Stefaniak, and R. S. Tobias, *Z. Naturforsch. B*, 25, 1088 (1970).

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Two Magnetically Subnormal Copper Halide Complexes with 1,8-Naphthyridine

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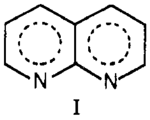
The compounds (1,8-naphthyridine)copper(II) chloride and the corresponding bromide have been prepared and characterized using magnetic properties and ir and visible spectra. The compounds are dimeric in the solid state and probably have square-pyramidal coordination at the metal atom.

Introduction

These laboratories have been concerned for some years with ligands having two basic groups separated by only a single atom (*e.g.*, acetate ion) which have the capability of forming a strained four-membered ring chelate or of bidentately bridging two metal atoms as in a wide variety of copper carboxylates. Among the more readily available ligands in this class are the negatively charged ions acetate, amidinate, and the anions of 2-pyridone and 1,3-diphenyltriazene. 1,8-Naphthyridine (I) is one of the rare neutral molecules in this class. Hendricker[1-5] and coworkers have recently done a great deal of work on coordination of 1,8-naphthyridine and



I

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(1) D. G. Hendricker and T. E. Reed, *Inorg. Chem.*, 8, 685 (1969).

(2) R. L. Bodner and D. G. Hendricker, *Inorg. Chem.*, 9, 1255 (1970).

(3) D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, 9, 273 (1970).

its derivatives. We report here the first examples of magnetically subnormal complexes of this ligand and discuss some possible structures for the new compounds.

Experimental Section

1,8-Naphthyridine (Hereafter Abbreviated NN). This compound was prepared by the method of Paudler and Kress.[6,7] Starting materials used were practical grade from various sources and were used without further purification. The crude products were purified by vacuum sublimation.

(1,8-Naphthyridine)copper(II) Chloride and Bromide, Cu(NN)Cl_2 and Cu(NN)Br_2. A solution of 0.5 mmol of the appropriate copper halide in 10 ml of 95% ethanol was heated to about 70° and 0.5 mmol of NN was added. The solution was then cooled to room temperature before filtering the precipitate. The product was washed with a small amount of 95% ethanol and dried over calcium chloride. Analyses are as follows.

	% calcd				% found			
Compd	Cu	C	H	X	Cu	C	H	X
$Cu(C_8H_6N_2)Cl_2$	24.01	36.31	2.29	26.80	23.91	36.34	2.18	26.61
$Cu(C_8H_6N_2)Br_2$	17.97	27.18	1.71	45.21	17.84	27.78	1.68	45.18

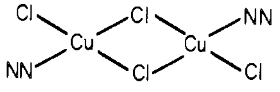
Carbon and hydrogen analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Copper analyses were done either iodometrically or by titration with EDTA. Chloride and bromide analyses were carried out by passing a solution of the compound through a cation exchanger and titrating the resultant acid with standard sodium hydroxide.

Infrared spectra were obtained on a Beckman Model IR-20 spectrometer using pressed KBr pellets. Spectra were calibrated at intervals using a polystyrene strip. Electronic spectra were obtained using a Cary 14 spectrophotometer; diffuse reflectance spectra were taken using the Cary 1411 diffuse reflectance accessory.

Magnetic susceptibilities were determined by the Gouy method using apparatus which has been described elsewhere.[8] X-Ray powder data were taken using a Philips powder camera of diameter 114.6 mm.

Discussion

The X-ray powder diffraction patterns of these two compounds in the solid state show them to be crystalline and isomorphous. The bromide has slightly larger dimensions as would be expected. The infrared spectra of the two compounds are also identical except in the region 350-250 cm^{-1} where the bands characteristic of the Cu-Cl bond appear. This Cu-Cl stretching pattern indicates the presence of both bridging and terminal chloride ions. Compounds containing only singly bonded (terminal) chloride ligands generally display only a single rather broad absorption in this region. For example, $Cu(NN)_2Cl_2$ which contains only terminal chlorides[9] has a single broad absorption centered at 285 cm^{-1}. When both terminal and bridging (doubly bonded) chlorides are present, three or four somewhat sharper bands generally occur in this region. $CuCl_2 \cdot 2$-pyridone, which has both bridging and terminal chlorides,[10] has four sharp bands in this general region. Other workers have made similar observations.[11,12] Cu(NN)Cl_2 has three sharp bands in this region, at 281, 291, and 301 cm^{-1}. The corresponding bromide is transparent at these points; Cu-Br stretching frequencies vary greatly but have been generally reported at frequencies below 250 cm^{-1}.[13,14] The spectrum of the chloride suggests that the complex contains a halide bridged dimeric unit of the type shown in II, where NN may or may not be chelated to copper.



II

Table I. Magnetic Susceptibility of Cu(NN)Cl_2 as a Function of Temperature[a]

T, °K	$10^6(\chi_m - N_\alpha)$, cm^3 mol^{-1} Obsd	Calcd	μ_{eff}, BM Obsd	Calcd[b]
86	1451	1455	1.00	1.00
109	1635	1650	1.19	1.20
121	1669	1677	1.27	1.27
139	1658	1665	1.36	1.36
159	1604	1612	1.43	1.43
181	1536	1536	1.49	1.49
202	1462	1452	1.54	1.54
225	1377	1370	1.57	1.57
248	1299	1285	1.61	1.60
271	1221	1213	1.63	1.62
291	1152	1152	1.64	1.64

[a] $N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. Diamagnetic corrections taken from B. Figgis and J. Lewis, *Tech. Inorg. Chem.*, 4, 142 (1965). $\mu_{eff} = 2.828\sqrt{(\chi_m - N_\alpha)T}$. [b] Parameters given in Table III.

In many cupric chlorides such dimers are linked together by sharing of the chlorides between dimers.[10,15] Such compounds are usually magnetically normal down to near liquid helium temperatures. In contrast the two complexes described here are magnetically anomalous at room temperature, and the magnetic susceptibility varies as does that of cupric acetate monohydrate as a function of temperature. Tables I and II list observed and calculated values of $(\chi_m - N_\alpha)$ and μ_{eff} as a function of temperature for Cu(NN)Cl_2 and Cu(NN)Br_2. The calculated values have been obtained using the equation first proposed by Bleaney and Bowers[16] to describe the magnetic properties of cupric acetate monohydrate and later discussed in detail by Figgis and Martin.[17] The equation was used in the form $\chi_m T = 0.125g^2[1 + {}^1/_3 e^{-J/kT}]^{-1} + N_\alpha T$. Computer fitting of this equation gives the values shown in Table III for the parameters g, J (the singlet-triplet separation), and T_c, the temperature of maximum susceptibility. The magnetic data are thus clearly consistent with the presence of isolated binuclear units in the crystalline compounds. The slightly larger value of $|J|$ observed for the bromide complex is consistent with the hypothesis of halide bridging[18,19] although in some instances $|J|(\mathrm{Br}) < |J|(\mathrm{Cl})$ has been observed.[20]

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[4] T. E. Reed and D. G. Hendricker, *Inorg. Chim. Acta*, 4, 471 (1970).

[5] R. L. Bodner and D. G. Hendricker, *Inorg. Nucl. Chem. Lett.*, 6, 421 (1970).

[6] W. W. Paudler and T. J. Kress, *J. Org. Chem.*, 32, 832 (1967).

[7] W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, 4, 1284 (1967).

[8] R. Colton, *U. K. At. Energy Auth., Res. Group, Rep.*, AERE-R4186 (1963).

[9] E. L. Enwall, K. Emerson, G. D. Smith, and A. Emad, submitted for publication.

[10] C. C. Houk and K. Emerson, *J. Inorg. Nucl. Chem.*, 30, 1493 (1968).

[11] R. Whyman and W. E. Hatfield, *Inorg. Chem.*, 6, 1859 (1967).

[12] W. H. Watson, *Inorg. Chem.*, 8, 1879 (1969).

[13] R. Colton and J. H. Canterford, "Halides of the First Row Transition Elements," Wiley-Interscience, New York, N. Y., 1969, pp 512-515, and references therein.

[14] D. M. Adams, "Metal-Ligand and Related Vibrations," E. Arnold, London, 1967, pp 54, 58.

[15] R. D. Willett and R. Rundle, *J. Chem. Phys.*, 40, 838 (1964).

[16] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, 214, 451 (1952).

[17] B. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

[18] C. G. Barraclough and C. F. Ng, *Trans. Faraday Soc.*, 60, 836 (1964).

[19] R. W. Adams, C. G. Barraclough, R. L. Martin, and G. Winter, *Aust. J. Chem.*, 20, 235 (1967).

[20] A. P. Ginsberg, R. C. Sherwood, R. W. Brookes, and R. L. Martin, *J. Amer. Chem. Soc.*, 93, 5927 (1971); *Inorg. Chem.*, 11, 2884 (1972).

Table II. Magnetic Susceptibility of $Cu(NN)Br_2$ as a Function of Temperature[a]

	$10^6(\chi_m - N_\alpha)$, $cm^3\ mol^{-1}$		μ_{eff}, BM	
T, °K	Obsd	Calcd[b]	Obsd	Calcd[b]
90	527	441	0.62	0.56
110	702	655	0.79	0.76
115	735	698	0.82	0.80
120	790	743	0.87	0.84
145	892	893	1.02	1.02
167	952	967	1.13	1.14
192	989	1001	1.23	1.24
200	998	1003	1.26	1.27
216	997	1002	1.31	1.31
230	989	994	1.35	1.35
248	979	978	1.39	1.39
270	954	953	1.44	1.44
290	915	926	1.46	1.47

[a] $N_\alpha = 60 \times 10^{-6}\ cm^3\ mol^{-1}$. Diamagnetic corrections taken from B. Figgis and J. Lewis, *Tech. Inorg. Chem.*, 4, 142 (1965). $\mu_{eff} = 2.828\sqrt{(\chi_m - N_\alpha)T}$. [b] Parameters given in Table III.

Table III. Magnetic Parameters Fitted for $Cu(NN)Cl_2$ and $Cu(NN)Br_2$

Compd	g	J, cm^{-1}	T_c, °K
$Cu(NN)Cl_2$	2.11	−139	125
$Cu(NN)Br_2$	2.09	−228	205

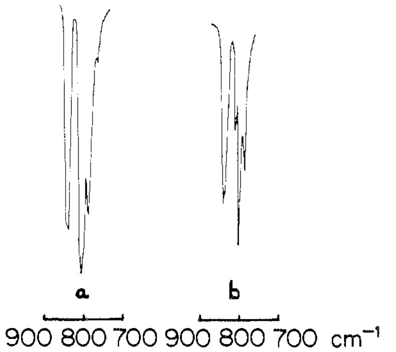

Figure 1. (a) Ir spectrum of $Cu(NN)_4(ClO_4)_2$. (b) Ir spectrum of $Cu(NN)_2(NO_3)_2$.

There are at least three possible coordination geometries for the core dimer: trigonal bipyramidal, square pyramidal, and square planar. Examples of dimers in the first and second configurations have recently been reported by Hatfield[21,22] and his coworkers. The compounds reported here appear from the ir electronic spectra to be tetragonal; a square-pyramidal geometry is also suggested by the ir spectrum.

$Cu(NN)Cl_2$ has its peak absorption in the d-d transition region at 13,250 cm^{-1}, too high in energy for a trigonal-bipyramidal geometry, even allowing for the ligand field effects of coordination by the NN molecule. The corresponding bromide absorbs at 13,160 cm^{-1}, slightly lower in energy as would be expected. Either square-planar or square-pyramidal complexes would be expected to absorb in this region.[23] The square-planar complex $Cu(NN)Cl_2$, with equal numbers of chlorine and nitrogen atoms coordinated,[9] has a broad d-d band which peaks at 14,800 cm^{-1}. The slightly lower energy of the band in $Cu(NN)Cl_2$ is probably due to the coordination of three chlorides to copper instead of only two.

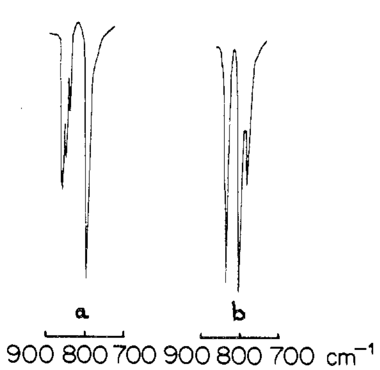

Figure 2. (a) Ir spectrum of $Cu(NN)Cl_2$. (b) Ir spectrum of $Cu(NN)_2Cl_2$.

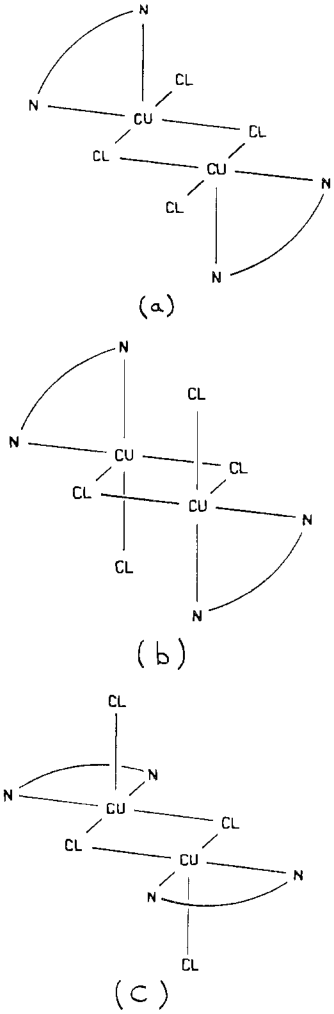

Figure 3. Possible structures of $Cu_2(NN)_2X_4$ dimers.

The ir spectra of NN in these and a number of other compounds have been examined and compared in detail. Hendricker and coworkers have listed a number of bands[2] in the infrared region which they regard as diagnostic of NN coordination. Observations in this laboratory on a large number of NN complexes, some prepared originally here and some prepared by Hendricker, indicate clearly that one cannot select one band or even a small number of bands in the ir spectrum as indicative of the mode of coordination of NN.[24] The bands between 750 and 900 cm^{-1} are especially sensitive to geometry and mode of coordination of the NN; these bands have been assigned as C-H bending and skeletal stretching modes.[3] When compounds have similar modes of

(21) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, 10, 1061 (1971).

(22) V. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, in press.

(23) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 3, 841 (1964).

(24) A. Emad, Thesis, Montana State University, 1971.

coordination, their spectra in this region are usually very similar. An example of this is shown in Figure 1. Cu$(NN)_4(ClO_4)_2$ and $Cu(NN)_2(NO_3)_2$ were originally prepared by Hendricker and coworkers[5,25] and are believed to have similar dodecahedral coordination geometries. As can be seen in Figure 1, the spectra are practically identical except for a slight change in the band at 805 cm^{-1}. This may be due to a nitrate bending mode in this region.

In Figure 2 the bands for $Cu(NN)_2Cl_2$ and $Cu(NN)Cl_2$ are compared in the same region. X-Ray diffraction of Cu$(NN)_2Cl_2$ has shown it to be a square-planar complex with monodentately coordinated NN.[9] The difference between the two spectra is quite striking. Now if the complex under discussion, $Cu(NN)Cl_2$, has square-planar geometry, it must have monodentate coordination of the NN, and hence very similar spectra would be expected. The extreme difference between the spectra thus suggests that the NN is bidentate and hence that the coordination in the two complexes reported here is probably square pyramidal.

Three geometries for the dimer are possible, depending on whether one or two chlorine atoms are in trans positions with respect to NN. The possible arrangements are shown in Figure 3. The structure of Figure 3b occurs in a copper complex of dimethylglyoxime whose structure was determined by Svedung.[26] However, in contrast to the compounds reported here, this complex follows a Curie law with μ_{eff} = 1.80 BM down to liquid nitrogen temperatures. This may be because the two square-planar units which compose the dimer are only very weakly interacting as indicated by the long plane-to-plane distance of 2.70 Å; bis(α-picoline)copper(II) chloride and bromide have similar very weak bonds between square-planar units and magnetic properties very similar to those of the dimethylglyoxime complex.[22,27] Figure 3b thus seems unlikely for the two compounds described here, but either Figure 3a or 3c will adequately explain all their physical properties.

In summary, these compounds appear from their magnetic and spectral properties to be halide-bridged dimers with square-pyramidal coordination at the metal atoms. Dimers are formed by sharing edges of the square base of the pyramidal coordination sphere. The additional sharing of halides between dimers which is usually found in such compounds may be prevented in this case by the bulky naphthyridine group.

Registry No. $Cu(NN)Cl_2$, 36926-70-2; $Cu(NN)Br_2$, 36926-71-3.

Acknowledgments. The authors wish to thank Professor William E. Hatfield of the University of North Carolina for permission to quote ref 22 in advance of publication. We are also indebted to the Chemistry Department at Washington State University, which permitted the use of its equipment to obtain some of the diffuse reflectance spectra.

(25) D. G. Hendricker and R. J. Foster, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 214.

(26) D. H. Svedung, *Acta Chem. Scand.*, 23, 2865 (1969).

(27) D. Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chim. Acta*, 5, 257 (1971).

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Some Mixed-Ligand Complexes of Copper(II)

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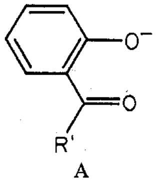
Bis(salicylaldehydato)copper(II), $(sal)_2Cu$, reacts with 1 mol of the amine $H_2NCH_2CH_2NR_2$ to give rise to complexes of formula $(sal)(salNR_2)Cu$ where $salNR_2$ is the Schiff base derived from sal and $H_2NCH_2CH_2NR_2$. Similar reactions also occur with bis(2-hydroxyacetophenonato)copper(II). The mixed-ligand complexes are characterized using analytical, infrared, and molecular weight data. They have normal magnetic moments. On the basis of electronic spectra it is suggested that they have pentacoordinated geometry. When these mixed-ligand complexes are treated with HCl or HBr, the bidentate moiety (*e.g.*, sal) is replaced by halide ion: the resultant complexes being planar. A mechanism for this reaction is suggested. From the halide, the corresponding nitrate and perchlorate can be obtained by double decomposition. The probable structures of these species are discussed in the light of conductivity, infrared, magnetic, and electronic spectral data.

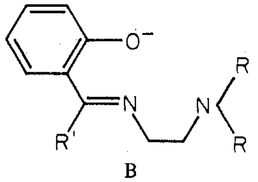
Introduction

Bis(salicylaldehydato)nickel(II) dihydrate and its homologs smoothly react[1,2] with 1 mol of N,N-disubstituted ethylenediamine to give rise to dimeric complexes of the general formula $A_2B_2Ni_2$ in which the A fragments act as bridges. These complexes are either pseudooctahedral (B unit is tridentate) or five-coordinate (B unit is bidentate with free terminal nitrogen) or an equilibrium mixture of the two depending on the conditions.[1,2] The present work was undertaken in order to explore the synthesis, structure, and reactions of the corresponding mixed-ligand complexes of copper(II). We were particularly encouraged by a report[3] due to Pfeiffer, *et al.*, stating that $(sal)_2Cu$ reacts with



A

R' = H, sal
R' = CH_3, hac



B

R' = H, $salNR_2$
R' = CH_3, $hacNR_2$

(1) T. S. Kannan and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, 6, 903 (1970).

(2) R. H. Balundgi, T. S. Kannan, and A. Chakravorty, *Inorg. Chim. Acta*, in Press.

(3) P. Pfeiffer and H. Krebs, *J. Prakt. Chem.*, 155, 77 (1940).