

coordination, their spectra in this region are usually very similar. An example of this is shown in Figure 1. $\text{Cu}(\text{NN})_4(\text{ClO}_4)_2$ and $\text{Cu}(\text{NN})_2(\text{NO}_3)_2$ 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 $\text{Cu}(\text{NN})_2\text{Cl}_2$ and $\text{Cu}(\text{NN})\text{Cl}_2$ are compared in the same region. X-Ray diffraction of $\text{Cu}(\text{NN})_2\text{Cl}_2$ 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, $\text{Cu}(\text{NN})\text{Cl}_2$, 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 $\mu_{\text{eff}} =$

(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).

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. $\text{Cu}(\text{NN})\text{Cl}_2$, 36926-70-2; $\text{Cu}(\text{NN})\text{Br}_2$, 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.

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

Contribution from the Department of Chemistry, Indian Institute of Technology, Kanpur-16, India

Some Mixed-Ligand Complexes of Copper(II)

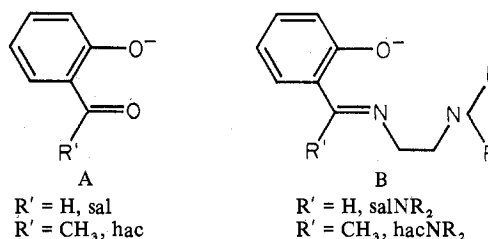
R. H. BALUNDGI and A. CHAKRAVORTY*

Received June 6, 1972

Bis(salicylaldehydato)copper(II), $(\text{sal})_2\text{Cu}$, reacts with 1 mol of the amine $\text{H}_2\text{NCH}_2\text{CH}_2\text{NR}_2$ to give rise to complexes of formula $(\text{sal})(\text{salNR}_2)\text{Cu}$ where salNR_2 is the Schiff base derived from sal and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NR}_2$. 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 $\text{A}_2\text{B}_2\text{Ni}_2$ 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 reac-



tions of the corresponding mixed-ligand complexes of copper(II). We were particularly encouraged by a report³ due to Pfeiffer, *et al.*, stating that $(\text{sal})_2\text{Cu}$ reacts with

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

(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.

Table I. Characterization Data

Compound	Mp, ^a °C	% C		% H		% N		% Cu ^b	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
(sal)(salNMe ₂)Cu	208-209	57.51	57.70	5.36	5.28	7.45	7.56	16.90	16.81
(sal)(salNEt ₂)Cu	137-138 dec	59.46	59.19	5.99	5.69	6.93	6.87	15.73	15.78
(sal)(salNHEt)Cu	168-169	57.51	57.40	5.36	5.14	7.45	7.69	16.90	16.95
(hac)(hacNMe ₂)Cu	166-167	59.46	59.33	5.99	5.86	6.93	7.15	15.73	15.61
(hac)(hacNEt ₂)Cu	135-136	61.18	60.90	6.48	6.69	6.48	6.50	14.72	15.00
(salNEt ₂) ₂ Cu	44	62.19	61.95	7.63	7.39	11.15	11.36		
(Cl)(salNMe ₂)Cu ^c	164-166	45.52	45.30	5.24	5.21	9.65	9.50	21.89	21.91
(Br)(salNMe ₂)Cu	181-182	39.46	39.20	4.52	4.70	8.37	8.50		
(NO ₃)(salNMe ₂)Cu	201-202 dec	41.70	41.65	4.77	4.73	13.26	13.50		
(Cl)(salNEt ₂)Cu	185-187	49.05	49.18	6.02	5.87	8.80	9.00	20.05	19.93
(Br)(salNEt ₂)Cu	165-167	43.03	43.68	5.24	5.45	7.72	7.83	17.51	17.48
[(H ₂ O)(salNEt ₂)Cu]ClO ₄ ·2H ₂ O ^d	200-202 dec							14.56	14.81
[(H ₂ O)(salNEt ₂)Cu]ClO ₄	200-202 dec							15.56	15.80

^a All melting points are uncorrected. ^b Copper was estimated as CuNCS. ^c Per cent chloride was estimated as AgCl: calcd, 12.21; found, 12.34. ^d Loss in weight of water on drying at 100° for 5 hr at 5mm. Per cent loss of 2 H₂O: calcd, 8.26; found, 8.70.

H₂NCH₂CH₂NEt₂ to give rise to a green complex of empirical formula (sal)(salNEt₂)Cu.

Results and Discussion

Syntheses. We are able to reproduce Pfeiffer's work³ which consists of heating (sal)₂Cu and Et₂NCH₂CH₂NH₂ in the absence of any solvent. However, we have found that heating to reflux a mixture of A₂Cu and the amine taken in a 1:1 molar ratio in toluene provides an efficient, neat, and general method for the syntheses of mixed-ligand complexes of the formula ABCu. In Table I are presented analytical data of these complexes together with those of other complexes discussed in this paper. In only one complex—abbreviated as (sal)(salNHEt)Cu—the two substituents of the terminal nitrogen are different, *viz.*, H and Et.

When A₂Cu is treated with amine in the molar ratio 1:2 in boiling toluene, the bis complexes of general formula B₂Cu are obtained in good yield. Contrary to Pfeiffer's report³ the complex (salNEt₂)₂Cu is obtainable. Several bis complexes of the same general type are already reported⁴ by Sacconi, *et al.* We shall not consider the bis complexes any further except where such considerations are required for structural elucidation of the mixed species. Interestingly when a 1:1 mixture of A₂Cu and B₂Cu is heated in toluene, the mixed-ligand complex is readily obtained.

Infrared Spectra. The ABCu complexes systematically show three infrared bands in the region 1570-1650 cm⁻¹ (Table II). The C=O and C=N stretches are respectively at 1615-1640 and 1595-1625 cm⁻¹. The third band at 1578-1600 cm⁻¹ is assigned to aromatic vibration. The identification of C=O frequencies is facilitated by the fact that it is absent in the bis complexes and in XBCu described later.

Electronic Spectra and Stereochemistry. The complex (sal)(salNEt₂)Cu will be considered first. Its cryoscopic molecular weight in benzene is 430 ± 20. The complex is thus monomeric (calculated mol wt 404) in striking contrast to the dimeric nickel(II) analog.² Depending on whether the NEt₂ group is coordinated or not, the complex can be either penta- or tetracoordinated. An electronic band at ~13,500 cm⁻¹ with a shoulder at higher energy is systematically observed in the solid state (Nujol mull) in benzene, chloroform, pyridine, and ethanol solutions (Figures 1 and 2). On the basis of the observed spectra we conclude that there are no significant structural changes in going from the solid state to the solution phase even when the solvent is a highly potent donor. This suggests a tightly bound structure⁵ to which

Table II. Some Infrared Frequencies (cm⁻¹)^a

Compound	Assignment		
	ν _{C=O}	ν _{C=N}	Aromatic
(sal)(salNMe ₂)Cu	1640	1625	1594
(sal)(salNEt ₂)Cu	1640	1625	1598
(sal)(salNHEt)Cu ^b	1642	1625	1598
(hac)(hacNMe ₂)Cu	1615	1595	1580
(hac)(hacNEt ₂)Cu	1620	1600	1578
(salNEt ₂) ₂ Cu		1625	1600
(Cl)(salNMe ₂)Cu		1625	1595
(NO ₃)(salNMe ₂)Cu		1625	1595
[(H ₂ O)(salNEt ₂)Cu]ClO ₄ ·2H ₂ O ^c		1625	1594

^a Measurements were made in KBr disk, in Nujol mull, and also in carbon tetrachloride where solubility permitted; the spectra did not depend on the phase. ^b A band at 3125 cm⁻¹ is assigned to N-H stretch. ^c A broad medium absorption at 3450 cm⁻¹ is due to H₂O; ClO₄⁻ shows an intense broad absorption at 1100 cm⁻¹.

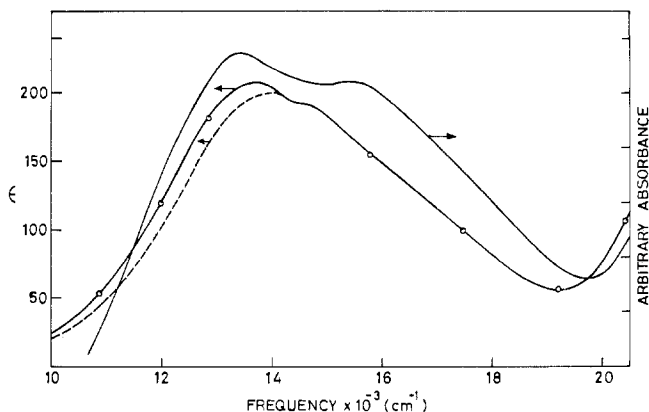


Figure 1. Electronic spectra of (sal)(salNEt₂)Cu: —, Nujol mull; - - - -, chloroform solution; - · - ·, pyridine solution.

solvent coordination cannot be readily accommodated. On this count we consider a planar structure unlikely. It is proposed that the complexes have a trigonal-bipyramidal structure C. The tridentate ligand is believed to span an edge rather than a face since the two nitrogen atoms are separated by only two carbon atoms. In octahedral bis complexes of nickel(II) of the type B₂Ni the ligand is known⁶ to span meridionally.

The spectral behavior of the remaining mixed-ligand complexes (Table III) is quite similar to that of (sal)(salNEt₂)Cu

(5) V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr.*, 25B, 2254 (1969).

(6) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, 4, 818 (1965).

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

Table III. Electronic Spectral and Magnetic Data of ABCu Complexes^a

Compound	Electronic spectra ^b			μ_{eff} of solids, BM
	Nujol mull	Chloroform	Pyridine	
(sal)(salNMe ₂)Cu	14,600, 16,660 sh	14,100 (274), 14,660 (194)	13,900 (265), 15,900 (192) sh	1.85
(sal)(salNEt ₂)Cu	13,300, 15,500 sh	13,700 (208), 14,800 (190) sh	13,900 (200), 14,800 (190) sh	1.85
(sal)(salNHEt)Cu	15,600, 17,850 sh	14,700 (238), 15,800 (204) sh	14,500 (275), 15,400 (255) sh	1.82
(hac)(hacNMe ₂)Cu	14,300, 16,600	14,300 (206), ^c 16,000 (216) ^c	14,300 (227), 16,100 (187) sh	1.91
(hac)(hacNEt ₂)Cu	14,000, ^b 16,400 ^b	13,900 (177) sh, 16,000 (242)	14,000 (213), 16,000 (196) sh	1.87

^a All measurements were made at room temperature (300°K); sh = shoulder. ^b Frequencies are in cm⁻¹; figures in parentheses refer to extinction coefficients in l. mol⁻¹ cm⁻¹. ^c Broad.

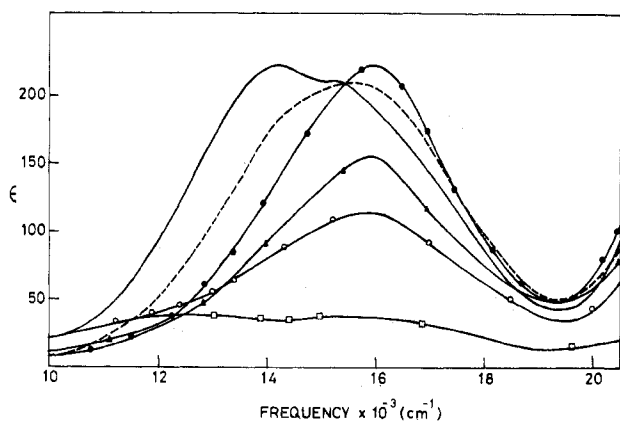
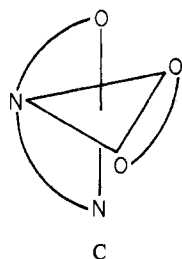


Figure 2. Electronic spectra of (sal)(salNEt₂)Cu with varying amounts of HCl in aqueous ethanol. (sal)(salNEt₂)Cu:HCl molar ratios: —, 1:0; ---, 1:0.5; -●-●-, 1:1; -▲-▲-, 1:2; -○-○-, 1:3; -□-□-, 1:4.



and a trigonal-bipyramidal structure is proposed for all the ABCu complexes.^{6a} The ligand field spectra of these chelates are strikingly like those⁷ of other pentacoordinated copper(II) complexes derived from Schiff bases. It is interesting to note that while the mixed-ligand nickel(II) complexes^{1,2} dimerize to achieve partial or complete pseudo-octahedral coordination around nickel(II), the copper(II) species remain monomeric with a stable pentacoordinated geometry. Similar differences in the stereochemical preferences of copper(II) and nickel(II) have been observed in other cases.⁷⁻¹⁰

(6a) Note Added in Proof. The three-dimensional X-ray structure of (sal)(salNMe₂)Cu has now been determined by us (R. Tewari, R. C. Srivastava, R. H. Balundgi, and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, in press). The coordination geometry is distorted square pyramidal rather than trigonal bipyramidal. The lack of solvent coordination is due to steric factors.

(7) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

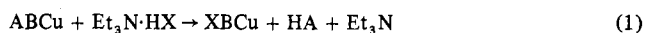
(8) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1865 (1970).

(9) J. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

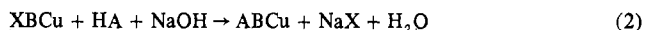
(10) P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, **89**, 6131 (1967).

The magnetic moments of the ABCu complexes uniformly lie close to 1.85 BM (Table III).

Reactions. In order to examine whether the terminal nitrogen in the B fragment of ABCu could be protonated with consequent delinking from the metal, several mixed-ligand complexes were allowed to react with NEt₃·HX (X = Cl, Br) in dry benzene in a 1:1 ratio. A reaction did occur but no [CuABH] X species could be isolated. In every case the bidentate A moiety was rejected and crystalline complexes of composition XBCu were obtained



These smoothly reacted with HA in alkaline medium to regenerate the ABCu complex



Reaction 2 does *not* occur when alkali is excluded. The XBCu complexes have normal magnetic moments and are essentially nonconducting in nitromethane (Table IV). Sacconi, *et al.*, have reported⁴ the electronic spectra of some XBCu complexes obtained by a different synthetic route. Our results are in full accord with the proposed⁴ planar structure. A few other XBCu complexes are described elsewhere.^{11,12} Some corresponding nickel(II) complexes are also known.¹³

Reaction 1, though very convenient for synthetic purposes, may proceed by a heterogeneous pathway since Et₃N·HX and XBCu remain in suspension. We have observed that when 1 mol of HCl is added to 1 mol of (sal)(salNEt₂)Cu in 95% ethanolic medium, the reaction



occurs quantitatively and "instantaneously." The visible spectrum (Figure 2) of the reaction mixture is superposable on the spectrum of (Cl)(salNEt₂)Cu in 95% ethanol. The only crystallizable material that can be isolated from the reaction mixture is (Cl)(salNEt₂)Cu. The presence of HA in the reaction mixture can also be demonstrated. When (sal)(salNEt₂)Cu is allowed to react with HCl in the ratio 1:0.5, the observed spectrum (Figure 2) clearly shows the presence of both (Cl)(salNEt₂)Cu and unreacted mixed complex. When a neutral halide such as Et₄NCl is mixed with (sal)(salNEt₂)Cu in ethanolic solution, the spectrum of the latter is not affected. This shows that protons are involved in the conversion ABCu → XBCu. A plausible mechanism for reaction 3 is that a proton attaches to the phenolic oxygen

(11) W. E. Hatfield and E. L. Bunger, *Inorg. Chem.*, **8**, 1194 (1969).

(12) J. Drummond and J. S. Wood, *J. Chem. Soc., Dalton Trans.*, 365 (1972).

(13) T. I. Benzer, L. Dann, C. R. Schwitzgebel, M. D. Tamburro, and E. P. Dudek, *Inorg. Chem.*, **10**, 2204 (1971).

Table IV. Electrical Conductivity and Magnetic Data of Complexes of the Type XBCu

Compound	Conductivity in nitromethane, ^a cm ² ohm ⁻¹ mol ⁻¹	μ_{eff} of solids, BM
(Cl)(salNMe ₂)Cu	3.4	1.81
(Br)(salNMe ₂)Cu	8.8	1.80
(NO ₃)(salNMe ₂)Cu	19.2	1.85
(Cl)(salNEt ₂)Cu	0.0	1.81
(Br)(salNEt ₂)Cu	8.6	1.86
[(H ₂ O)(salNEt ₂)Cu]ClO ₄ ·2H ₂ O	85.4	1.85

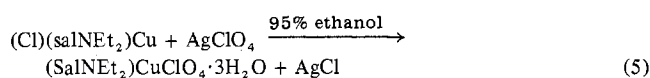
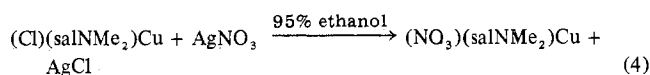
^a Measurements were made at 18° and solute concentrations were in the range (1–3) × 10⁻³ M.

of the A fragment followed by the detachment of the AH moiety and attachment of solvent (S) or X.

The reactivities of A and B chelates are strikingly different. Up to 1 mol of protons, only the A ring is removed. On increasing the amount of the acid further, the intensity of the (Cl)(salNEt₂)Cu band decreases and the absorption in the near-ir region increases probably due to the formation of solvated Cu²⁺ ions. However, the (Cl)(salNEt₂)Cu band does not disappear even when the ratio of ABCu:HCl reaches 1:3 (Figure 2). This shows that the removal of B ring proceeds by a reversible reaction whose equilibrium position does not lie completely in favor of the products.

We have also studied reaction 1 in an alcoholic medium in which the reaction is homogeneous. The reaction does not proceed to completion when ABCu:Et₃N·HX reaches 1:1; an equilibrium mixture is obtained instead. This is understandable since both Et₃N and A effectively compete for the proton.

By treating XBCu with appropriate silver salts it is possible to synthesize other species in which the BCu moiety remains intact, for example



The nitrate and the perchlorate can be readily isolated as crystals. Their magnetic and electrical conductivity (in nitromethane) data are shown in Table IV. The perchlorate is essentially a 1:1 electrolyte.¹⁴ This is also in accord with the infrared spectrum of the solid in which a broad and very strong band (with some ill-defined structure) characteristic of ionic perchlorates appears at ~1100 cm⁻¹. When heated, the perchlorate readily (100°, 5 mm) loses two of the three molecules of water and the resulting product (salNEt₂)CuClO₄·H₂O still shows an ionic perchlorate in the infrared spectrum. It is concluded that in the perchlorates the coordination sphere of copper has only the B ligand and water and the probable formulation of the trihydrate is [(H₂O)(salNEt₂)Cu]ClO₄·2H₂O. When the monohydrate is recrystallized from water, the trihydrate is again obtained. The nitrate shows appreciable conductivity (Table IV) in nitromethane although the conductivity is much lower than that of the perchlorate showing that the equilibrium (6) exists

$$\text{NO}_3\text{BCu} + n\text{CH}_3\text{NO}_2 \rightleftharpoons \text{BCu}(\text{CH}_3\text{NO}_2)_n^+ + \text{NO}_3^- \quad (6)$$

in solution. The mode of bonding¹⁵ (whether monodentate or bidentate) of the NO₃ group in NO₃BCu could not be confidently decided on the basis of infrared spectra due to

(14) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(15) C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev., Chem. Soc.*, **25**, 289 (1971).

the presence of interfering bands of the B fragment. In chloroform solution the nitrate complex shows a single well-defined electronic band at 16,400 cm⁻¹ (ϵ 302). The shape and position of the band in the solid state are the same. The spectrum is quite different from those of the mixed-ligand species (Figure 1, Table III) but is significantly similar to those of the halo species (e.g., (Cl)(salNMe₂)Cu in chloroform shows a band at 15,600 cm⁻¹ (ϵ 344)). On this basis we suggest that the nitrate complex is grossly planar with a monodentate nitrate group.

The halide, nitrate, and perchlorate complexes dissolve in water to give rise to stable blue solutions which have identical electronic spectra (band at 15,900 cm⁻¹ (ϵ ~180)). Evidently in aqueous solution the species (H₂O)_nBCu⁺ alone is present.

Experimental Section

Preparation of Compounds. (a) **Mixed-Ligand Species.** The following general procedure was used. A₂Cu (0.005 mol) was suspended in 25 ml of toluene and to this was added 0.005 mol of the amine. The mixture was heated to reflux for 1 hr. The green solution was filtered. Crystals of (sal)(salNMe₂)Cu, (sal)(salNHET)Cu, and (hac)(hacNMe₂)Cu were obtained directly by cooling the filtrate. In the case of (sal)(salNEt₂)Cu and (hac)(hacNEt₂)Cu the filtrate was reduced to half its volume with subsequent addition of hexane. The green crystalline compounds were recrystallized from toluene or from toluene-hexane mixture. The yield in each case was ~90%.

(b) (salNEt₂)₂Cu was prepared by heating to reflux (sal)₂Cu (0.005 mol) with *N,N*-diethylethylenediamine (0.01 mol) in 25 ml of toluene for 1 hr. The solvent was stripped off completely. The oily residue was dissolved in the minimum quantity of hexane and the filtered solution was allowed to evaporate at room temperature. Large dark green crystals were formed in a few days. The crystals were washed with a small volume of hexane and dried. The complex is highly soluble in all common solvents and this makes its isolation somewhat difficult. In Nujol mull the complex shows an electronic band at 15,400 cm⁻¹ with a shoulder at ~17,000 cm⁻¹. In chloroform solution it shows a band at 15,800 cm⁻¹ (ϵ 207).

(c) **Reaction of (sal)₂Cu with (salNMe₂)₂Cu.** (sal)₂Cu (0.005 mol) and (salNMe₂)₂Cu⁺ (0.005 mol) were taken in 30 ml of toluene and heated to reflux for 2 hr. The solution was filtered and then cooled. Green crystals separated in 80% yield. The crystals were identical in all respects with (sal)(salNMe₂)Cu prepared by procedure (a).

(d) **XBCu (X = Cl, Br).** These were prepared by heating to reflux with simultaneous magnetic stirring a mixture of ABCu (0.005 mol) and Et₃N·HX (0.005 mol) in dry benzene (100 ml) for 4 hr. The crystalline product was collected by filtration and was recrystallized from chloroform-benzene mixture. The yield of the dark crystals was 60%. When (sal)(salNMe₂)Cu was replaced by (salNMe₂)₂Cu in the above preparation, the same complex, *viz.*, (X)(salNMe₂)Cu, was obtained.

(e) **Reaction of XBCu with the Sodium Salt of Salicylaldehyde.** Salicylaldehyde (0.005 mol) was dissolved in a solution of NaOH (0.005 mol) in 35 ml of ethanol. This solution was added to XBCu (0.005 mol) in 35 ml of alcohol. The mixture was heated to reflux for 2 hr followed by removal of solvent. The residue was extracted with toluene leaving behind NaX. Green crystals were obtained by concentrating and cooling the extract. Hexane was added where required (as under (a)).

(f) **Reaction of (salNEt₂)Cu with HCl.** (sal)(salNEt₂)Cu (0.002 mol) was dissolved in 95% ethanol, and 0.002 mol of HCl (0.047 *N*) solution in water was added. The mixture was allowed to evaporate at room temperature. The dark solid that separated was filtered and washed thoroughly with benzene. It was then recrystallized from a dichloromethane-benzene mixture. The yield of the final product was 80%. The compound was found to be identical in all respects with (Cl)(salNEt₂)Cu prepared by procedure (d).

For carrying out spectrophotometric experiments (Figure 2) a stock aqueous solution of HCl of strength 0.0470 *N* was prepared. This was taken in several parts: (i) 1.25 ml, (ii) 2.50 ml, (iii) 5.00 ml, (iv) 7.50 ml, and (v) 10.00 ml. Each part was separately diluted with 95% ethanol, the final volume being 50 ml. A 4.7-mg sample of (sal)(salNEt₂)Cu was dissolved in 5 ml of each of these solutions. The chelate:HCl ratios in these solutions are respectively 1:0.5, 1:1, 1:2, 1:3, and 1:4.

(g) **Reaction of (Cl)(salNMe₂)Cu with AgNO₃.** (Cl)(salNMe₂)Cu

(0.003 mol) was dissolved in 15 ml of ethanol and a solution of AgNO_3 (slightly in excess of 0.003 mol) dissolved in 25 ml of hot ethanol was added. The precipitate of AgCl was separated by filtration after warming the solution for a few minutes. From the filtrate ethanol was removed. The residue was dissolved in a minimum quantity of chloroform and benzene (15 ml) was added. On standing, black crystals of $(\text{NO}_3)(\text{salNMe}_2)\text{Cu}$ separated in 80% yield.

(h) Reaction of $(\text{Cl})(\text{salNEt}_2)\text{Cu}$ with AgClO_4 . Dry AgClO_4 (0.005 mol) was dissolved in 15 ml of 95% ethanol and this solution was added to a solution of $(\text{Cl})(\text{salNEt}_2)\text{Cu}$ (0.005 mol) in 15 ml of ethanol. The precipitated AgCl was filtered. The volume of the filtrate was reduced to 10 ml followed by the addition of water (30 ml) and the solution was stirred magnetically at room temperature. Blue crystals of the composition $[(\text{H}_2\text{O})(\text{salNEt}_2)\text{Cu}]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ started separating within 2 hr. The trihydrate when dried at 100° for 5 hr at 5 mm gave brown $[(\text{H}_2\text{O})(\text{salNEt}_2)\text{Cu}]\text{ClO}_4$.

Physical Measurements. Magnetic moments were studied using a Gouy balance described elsewhere.¹⁶ Electronic spectra were studied on a Cary Model 14 spectrometer. Solids were examined in finely dispersed hydrocarbon mulls sandwiched between quartz plates.

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Infrared spectra were recorded on a Perkin-Elmer 521 recording spectrometer. Conductivity measurements were made in nitromethane at 18° using a Systronics (India) bridge. Molecular weights were determined cryoscopically in thiophene-free dry benzene.

Registry No. $(\text{sal})_2\text{Cu}$, 14523-25-2; $(\text{hac})_2\text{Cu}$, 18898-20-9; $(\text{sal})(\text{salNMe}_2)\text{Cu}$, 37478-15-2; $(\text{sal})(\text{salNEt}_2)\text{Cu}$, 37478-16-3; $(\text{sal})(\text{salNAEt})\text{Cu}$, 37478-17-4; $(\text{hac})(\text{hacNMe}_2)\text{Cu}$, 37662-28-5; $(\text{hac})(\text{hacNEt}_2)\text{Cu}$, 37478-18-5; $(\text{salNEt}_2)_2\text{Cu}$, 37534-37-5; $(\text{Cl})(\text{salNMe}_2)\text{Cu}$, 37478-19-6; $(\text{Br})(\text{salNMe}_2)\text{Cu}$, 37478-20-9; $(\text{NO}_3)(\text{salNMe}_2)\text{Cu}$, 37478-21-0; $(\text{Cl})(\text{salNEt}_2)\text{Cu}$, 37478-22-1; $(\text{Br})(\text{salNEt}_2)\text{Cu}$, 37478-23-2; $[(\text{H}_2\text{O})(\text{salNEt}_2)\text{Cu}]\text{ClO}_4$, 37478-24-3.

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Magnetic Exchange in Oxalate- and Squarate-Bridged Nickel(II) Dimer Complexes

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Variable-temperature (4.2–290°K) magnetic susceptibilities were determined for one squarate-bridged and two oxalate-bridged nickel(II) dimers. Antiferromagnetic interactions were detected in both types of dimers; the oxalate-bridged dimers have $J \simeq -17 \text{ cm}^{-1}$, whereas the squarate-bridged dimer has $J \simeq -0.4 \text{ cm}^{-1}$. The magnetic exchange mechanism is discussed and symmetry considerations are delineated.

Introduction

Nickel(II) cluster compounds have been the focal points of several recent magnetic susceptibility studies.² Complexes have been found with antiferromagnetic exchange interactions as well as ferromagnetic interactions. In fact, linear trimeric bis(acetylacetonato)nickel(II) has been reported³ to have both ferromagnetic coupling ($J = +26 \text{ cm}^{-1}$) between adjacent nickel atoms and antiferromagnetic coupling ($J = -7 \text{ cm}^{-1}$) between the terminal nickel atoms. Linear-chain one-dimensional antiferromagnetism has been detected for CsNiCl_3 .⁴ Very recently Ginsberg^{2,5} reported the first example, in a cluster complex, of ferromagnetic exchange coupling between metal atoms linked by polynuclear bridges (thiocyanate groups) in $[\text{Ni}_2(\text{en})_4(\text{NCS})_2]\text{I}_2$.

Oxalate-bridged metal dimers have been known for some time.⁶ Crystal structures have been reported for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$,⁷ $\text{Cu}(\text{NH}_3)_2\text{C}_2\text{O}_4$,⁸ $(\text{NH}_4)_2[(\text{UO}_2(\text{C}_2\text{O}_4)_3]$,⁹

$\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$,¹⁰ and $[\text{Ru}_2(\text{py})_8(\text{C}_2\text{O}_4)](\text{BF}_4)_2$.¹¹ The oxalate bridge is planar and bis bidentate. Curtis has reported^{12,13} the preparation of various oxalate-bridged nickel dimers. In the following we report the results of a magnetic susceptibility study of some nickel dimers bridged either by oxalate or by squarate ($\text{C}_4\text{O}_4^{2-}$). We address ourselves to two main questions: "How will the magnetic interaction between the nickel(II) atoms compare between oxalate- and squarate-bridged dimers and what type of magnetic interaction will the oxalate triatomic bridge propagate, given the observation that the thiocyanate bridge leads to a net ferromagnetic interaction?" The latter question is relevant in that the thiocyanate-bridged nickel dimer is the only other triatomic-bridged nickel(II) complex studied magnetically.

Theory

The ground state of Ni(II) in an octahedral environment is orbitally nondegenerate and as such we represent intradimer magnetic interactions with the isotropic spin Hamiltonian

$$\hat{H} = -2J\hat{s}_1 \cdot \hat{s}_2 \quad (1)$$

Here J is the exchange integral and \hat{s}_1 is a spin operator. The

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