

The liberated proton has been calculated from the figure, which represents potentiometric titrations of aspartic acid with standard alkali in the absence and presence of metal ions at three different temperatures. No precipitation, was observed until pH of

		TABLE		
		35°	45°	55°
Pr(III)	$\log K_1$	5.639	5.632	—
	$\log K_2$	—	5.802	5.698
Gd(III)	$\log K_1$	5.643	—	—
	$\log K_2$	5.747	5.664	5.668

4.5 has been attained. At any pH between 3.0 to 4.5 the horizontal distances between the curves (obtained by titration of ligand directly and with metal corresponding to different temperatures) has been used to determine the additional base consumed or ligand complexed. From this value, \bar{n} has been calculated. Formation curves for the metal ligand system were plotted using \bar{n} and $-\log(\text{Asp})$ values. The stability constants were read directly from these formation curves at \bar{n} values of 0.5 and 1.5 respectively. Calvin and Melchoir⁶ extension of Bjerrum's⁷ method was used for calculation. The results are given in the table.

Thermodynamic functions :

The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of complexes formed have determined at 35° and were found to be -7.921 Kcal./mole, -46.87 Kcal./mole and -126.5 Kcal./deg./mole for Pr(III) aspartate and -7.927 Kcal./mole, -52.10 Kcal./mole and -143.4 Kcal./deg./mole for Gd(III) aspartate respectively.

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Studies in Copper(II) Chelates. Part VIII. Action of Ethylenediamine and Trimethylenediamine on some Copper(II) Chelates of Tridentate dibasic Schiff Bases

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WE describe here the results of our attempted synthesis of copper(II) mixed chelates of the type $[\text{Cu}(\text{en})(\text{SB})]$ (or $[\text{Cu}(\text{tn})(\text{SB})]$) (en = ethylenediamine; tn = trimethylenediamine; SBH_2 = tridentate dibasic schiff base e.g. glycine-salicylaldehyde, glycine-hydroxynaphthaldehyde etc.) by the action of en(or tn) on $[\text{Cu}(\text{SB})_2]$ or by the action of SBH_2 on $[\text{Cu}(\text{en})\text{aq}]$ (or $[\text{Cu}(\text{tn})\text{aq}]$). These reactions lead to N,N'-ethylene (or N,N'-trimethylene) bis(salicylaldiminato) copper (II)

Experimental

Procedure A :

Copper acetate (·001 mole) was taken in ethanol (20 ml) and to this was added a solution of the Schiff base^{1,2} (·001 mole in 30 ml hot ethanol). The mixture was refluxed for about 30 mins. A green, olive green or a yellow compound separated. Ethylenediamine or trimethylenediamine (·001 mole) was added and the mixture refluxed for 3-4 hrs. Products were purified, analysed for metal and nitrogen and examined microscopically and spectrophotometrically.

Procedure B :

The tridentate Schiff base^{1,2} (·001 mole in 30 ml ethanol) was added to the deep violet solution of copper acetate (·001 mole in 20 ml ethanol) and ethylenediamine (·001 mole) or trimethylenediamine, and the products treated as above.

Results and Discussion

Procedure A and procedure B constitute two straight forward routes to our projected goal. The reactions may lead to (1) mixed chelates ($[\text{Cu}(\text{en})(\text{SB})]$) formation; (2) ethylene of trimethylenebridged complexes, $[(\text{SB})\text{Cu}(\text{en})\text{Cu}(\text{SB})]$; or to (3) amine exchange. Analytical data given in Table I convince us that amine exchange occurs and we get copper(II) complexes of the quad adentate Schiff base of the amine and the appropriate hydroxyaldehyde as shown in (A) and (B).

Amine exchange reactions have been observed with bidentate mono basic Schiff base complexes of copper(II)^{3,4}, nickel(II)⁵, and also with quadridentate Schiff base complexes of copper(II)³. To our knowledge this is for the first time that an amine exchange reaction on a tridentate Schiff base complex is reported to yield a complex of a quadridentate Schiff base. The ease of the amine exchange, expectedly, depends on the substituent group (X) on

the aromatic ring of the aldehyde moiety. When C_6H_4 (*o*-OH) or CH_2-COO- —the amine exchange is quite easy. After refluxing the reactants for some time followed by cooling the quadridentate Schiff base complex separates in almost quantitative yield. When B is CH_2-COO- the amino acid (glycine) being

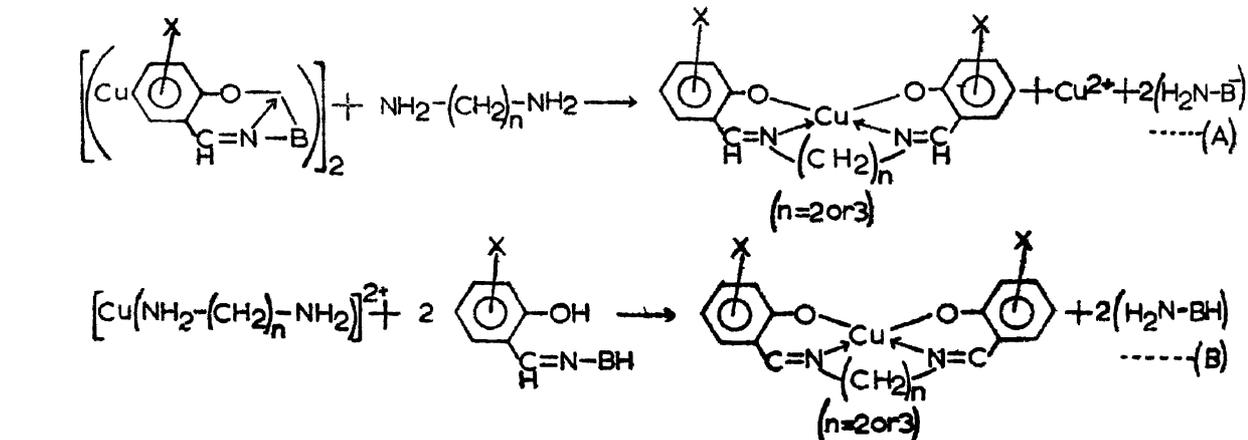


TABLE I—AMINE EXCHANGE REACTIONS OF

X	B	Amine	Preparative procedure	Analysis of the product % of Cu	% of N	Product**
H	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_5$	en	A B	19.0 (19.1)*	8.2 (8.4)	N,N' ethylenebis (salicylaldiminato) copper(II)
H	CH_2-COO-	en	A B	19.0 (19.1)	8.1 (8.4)	"
H	$C_6H_5(COO-)$	en	A B	19.2 (19.1)	8.2 (8.4)	"
5-Cl	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_5$	en	A B	15.4 (15.9)	7.16(7.03)	N,N' ethylenebis (5-chlorosalicylal-diminato) copper(II).
5-Cl	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_4(o-OH)$	en	A B	15.4 (15.9)	7.2(7.03)	"
5,6 benzo	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_5$	en	A B	14.8 (14.7)	6.3 (6.5)	N,N' ethylenebis(2-hydroxy-1-naphthaliminato) copper(II)
5,6 benzo	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_4(o-OH)$	en	A B	14.8 (14.7)	6.3 (6.5)	"
5,6 benzo	CH_2-COO-	en	A B	14.77(14.7)	6.4 (6.5)	"
5,6 benzo	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_5$	tn	A B	14.1 (14.3)	6.15(6.3)	N,N' trimethylene bis (2-hydroxy-1-naphthaliminato) copper(II).
5,6 benzo	$N = \overset{\text{O}}{\underset{ }{C}} - C_6H_4(o-OH)$	tn	A B	14.2 (14.3)	6.35(6.3)	"

* Calculated values are in parentheses.

** The amine-exchange product obtained via procedure B was established to be the same as that obtained via procedure A through microscopic and spectrophotometric comparison of the two products.

NOTES

insoluble in ethanol readily separates. This has been purified and identified through analysis and undepressed melting point of a mixture with an authentic sample. Amine exchange is also easy with a 5-chloro substituent on the aromatic ring of the aldehyde moiety. But when $X = H$, the reaction is rather slow and a large excess of the bidentate amine had to be added so as to obtain a reasonable yield of the copper(II) complex of the quadridentate Schiff base.

The copper(II) complexes of tridentate, dibasic Schiff bases are known to be dimeric and antiferromagnetic⁶, and are known to give in pyridine (py) monomeric square planar $[Cu(Py)(SB)]^7$. The interesting feature of the amine exchange reactions described herein (procedure A) is that in the starting Schiff base complex we have one hydroxyaldehyde moiety per copper(II) whereas in the final product we have two hydroxyaldehyde moieties per copper(II). This means that the two NH_2 -groups of 'en' or 'tn' have to attack two azomethine carbon atoms of two tridentate Schiff base units. If we assume a long *trans planar* disposition of the two hydroxyaldehyde moieties of the starting dimeric species it is certain that the 'en' or 'tn' NH_2 -s can not simultaneously bite the two widely separated *trans* azomethine carbon atoms. Instead it appears more likely and less strenuous for the 'en' or 'tn' NH_2 -s to bite one azomethine carbon resulting in the destruction of the dimer and this is then followed by the other NH_2 end of 'en' or 'tn' biting a second neighbouring azomethine carbon in solution. That this suggestion has some appeal is revealed from the following considerations. On coordination to a copper(II) the azomethine carbon becomes positive (δ^+) making it more susceptible to a nucleophilic attack by NH_2 -group of 'en' or 'tn'. In the free ligand also the azomethine carbon is expected to be distinctly though slightly positive because of electronegativity difference between carbon and nitrogen. It has been observed earlier^{4,8} that coordination is not the sole criterion for the polarisation of the azomethine carbon atom. In keeping with this we have observed a facile amine exchange on the Schiff



base alone when B is $N = C - C_6H_5$ and X is 5,6 benzo. Since in this case there is neither a metal complex involved nor any antiferromagnetic dimeric species the nucleophile does not have to resort to *trans* biting. The ready and facile amine exchange in the case of the free ligand indicates a similar path for the copper(II) complex also. In the complex surely the nucleophilic attack will be even more facilitated because the azomethine carbon becomes more positive due to coordination of the azomethine nitrogen to copper(II)⁸.

In conclusion we would like to note that synthesis of mixed chelates of the type $[Cu(en)(SB)]$ or $[Cu(tn)(SB)]$ via (a) reaction of 'en' or 'tn' with $[Cu(SB)]_2$ or via (b) reaction of $[Cu(en)aq]$ or $[Cu(tn)_2]$ with SBH_2 will remain a remote possibility.

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Thermodynamic Functions of F_2SNF , F_2SNCl and F_2SNBr from Spectroscopic Data

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THE extent of the reactivities of molecules may be ascertained from the knowledge of the thermodynamic functions of the molecules; the importance of ideal gas thermodynamic functions to equilibrium and kinetic phenomena is well known. It is almost impossible to obtain the thermodynamic properties of the electronically excited molecules and also some of the compounds in the ground state by experimental means, specifically in non-equilibrium situations, depending upon the range of temperature and pressure. Hence, only through theoretical calculations may one obtain information regarding the properties of these species. For such quantum statistical calculations, the vibrational and rotational data are needed, which at present can only be obtained from spectroscopic studies. Recently, the compounds, F_2SNF , F_2SNCl and F_2SNBr were prepared and their vibrational spectra have been reported in the literature¹. The assignment of the inplane and out-of-plane vibrations has also been made. Since these types of compounds are very difficult to prepare, thermodynamic functions of such compounds may not be determined easily by experimental means. Hence we thought it worthwhile to compute the thermodynamic functions of these molecules from the

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