

The introduction of the bulky phenanthroline was strongly affected by the greater ease with which a ligand could dissociate from the negatively charged complex than from a neutral complex when the incoming ligand was not providing much assistance.

Conclusion

Compared with the platinum(II) substitution reactions by unidentate and flexible bidentate ligands, those by phenanthrolines are slow. As with the other ligands, there are both direct and solvent paths to the prod-

uct. The latter path, however, is unusual in being second order, the result of the slower attack on the platinum by phenanthroline than by water. The reaction is unusually sensitive to the charge of the complex, with more negative charges giving faster rates. It is true that $\text{Pt}(\text{H}_2\text{O})\text{Cl}_3^-$ reacts a little faster than PtCl_4^{2-} , but not nearly as much faster as anticipated, considering that water is being replaced.²⁵ These facts seem to indicate that the character of the substitution is more dissociative than it is with other ligands.

(25) See ref 2, pp 379, 383.

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Medium-Ring Complexes. III. A Comparison of Planar and Pyramidal Copper(II) and Planar Nickel(II) Complexes Containing Seven- and Eight-Membered-Ring Diamines¹

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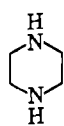
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The spectral properties of planar complexes of copper(II) and nickel(II) with 1,5-diazacyclooctane (daco) are compared to planar nickel(II) and planar and pyramidal copper(II) complexes with 1,4-diazacycloheptane (dach). The geometry of the chelate rings in the bis-dach complexes is discussed and the effects of conversion of $\text{Cu}(\text{dach})_2^{2+}$ complexes from four- to five-coordinated species are analyzed. The planar $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ has a λ_{max} in the visible spectrum at 505 m μ whereas the pyramidal $[\text{Cu}(\text{dach})_2\text{Cl}]\text{ClO}_4$ has a λ_{max} near 610 m μ . When other ligands occupy the apical position of the pyramidal complex, the maximum lies between these extremes. A spectrochemical series may be established based on the shift of the absorption maxima to lower energy as various ligands are added to the apical position: $\text{ClO}_4^- \sim \text{CH}_3\text{NO}_2 < (\text{CH}_3)_2\text{CO} < \text{CH}_3\text{CN} < \text{DMSO} \sim \text{NO}_3^- < \text{H}_2\text{O} < \text{HCONH}_2 \ll \text{SCN}^- \sim \text{Br}^- \sim \text{Cl}^-$.

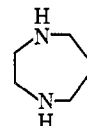
Introduction

Acylic molecules containing the grouping $\text{N}(\text{CH}_2)_n\text{N}$ in their structures are among the best characterized chelating agents for transition metal ions.²⁻⁹ However, the related cyclic diamines have not been studied extensively. Piperazine, the six-membered-ring diamine, does not form chelated bicyclic complexes with the smaller transition metal ions such as copper(II) and nickel(II) although complexes of palladium(II) and iridium(II) can be prepared.^{10,11} Assuming that the strain induced in the chelated structure would be reduced if additional methylene groups was introduced between the amine functions, the eight-membered-ring diamine 1,5-diazacyclooctane (daco)¹² and the seven-membered-ring diamine 1,4-diazacycloheptane

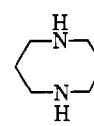
(dach) were examined as chelating agents for nickel(II) and copper(II).



piperazine



1,4-diazacycloheptane
homopiperazine
(dach)



1,5-diazacyclooctane
(daco)

(1) Abstracted in part from the Ph.D. Thesis of M. S. Hussain, University of California, Davis, Calif., 1968.

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When nickel(II) and copper(II) salts were treated with daco, planar complexes were obtained regardless of the anion or solvent present.¹² Nickel(II) complexes of dach were also planar. However, the geometry of the dach complexes of copper(II) was dependent on the solvent and the anions present, for both tetra- and pentacoordinated complexes could be prepared.¹³ Thus, a comparison of daco and dach complexes is advantageous since the local environment of the metal ions in the planar, four-coordinated bis complexes is similar, and variations in the physical and chemical properties of the two complexes can be attributed to

changes in coordination number. In addition, the spectral data may be particularly informative in that the ligand does not contain a π -electron system and all of the absorption maxima can be assigned to either d-d or ligand-to-metal transitions. In this study the molecular properties of daco and dach complexes of nickel(II) and copper(II) are compared by the use of infrared, ultraviolet, and visible absorption spectroscopy in aqueous and nonaqueous solvents, magnetic susceptibility, and electrolytic conductivity. The stability constants of the dach complexes are also compared with the daco complexes. The crystal structure of pyramidal nitratobis(1,4-diazacycloheptane)copper(II) nitrate will be reported shortly.¹⁴

Experimental Section

Materials.—Nickel(II) perchlorate hexahydrate and copper(II) perchlorate hexahydrate were obtained from the G. F. Smith Chemical Co.; copper(II) nitrate trihydrate, copper(II) bromide, copper(II) chloride dihydrate, nickel(II) chloride hexahydrate, and nickel(II) nitrate hexahydrate were obtained from Allied Chemical Corp. These compounds were used without further purification.

The nonaqueous solvents, nitromethane, acetonitrile, dimethyl sulfoxide, etc., used in the spectral analysis were spectroquality grade obtained from Matheson Coleman and Bell. The purity of these solvents was checked by vapor-phase gas chromatography and their water content was checked by infrared spectral analysis.

The seven-membered cyclic diamine, 1,4-diazacycloheptane (dach) or homopiperazine, was obtained from Aldrich Chemical Co. The preparation of the eight-membered cyclic diamine, 1,5-diazacyclooctane (daco), was discussed in a preceding paper.¹²

Bis-Amine Complexes of the Type $M(\text{dach})_2X_2$ ($M = \text{Ni(II)}$ or Cu(II) ; $X^- = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{or } \text{ClO}_4^-$).—The hydrated copper(II) or nickel(II) salts were shaken with 10–15 ml of 2,2-dimethoxypropane for 0.5 hr to remove water.^{15,16} The resulting solution was filtered and diluted with 10–12 ml of anhydrous ethanol. Excess ligand was dissolved in anhydrous diethyl ether and added slowly while stirring to the solution of metal ion. Usually the complexes precipitated immediately. The compounds were filtered by suction, washed several times with anhydrous ether, and finally washed with a 2:1 ether-ethanol mixture. Initial drying was accomplished in a vacuum desiccator and final drying was done by warming the compound to 60–65° on a vacuum line for 5–6 hr. The yields were about 85% and the analytical data are reported in Table I.

Bis-Amine Complexes of the Type $[M(\text{dach})_2X]Y$ ($X^- = \text{Cl}^-, \text{Br}^-, \text{or } \text{SCN}^-$; $Y^- = \text{ClO}_4^- \text{ or } \text{NO}_3^-$).—Complexes having two different anions were prepared by exchange of a perchlorate or nitrate with Cl^- , Br^- , or SCN^- or by mixing equimolar solutions of the corresponding complexes of the type $M(\text{dach})_2X_2$ in nitromethane.

$[\text{Cu}(\text{dach})_2\text{Br}]\text{ClO}_4$ was prepared by shaking $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ in warm, anhydrous methanol to which a small excess of solid lithium bromide had been added. This slurry was placed on an automatic shaker for 2–3 hr and the resulting solid was filtered. The precipitate was washed with a dilute methanolic solution of lithium bromide and finally with an ethanol-ether mixture. The drying of the precipitate was accomplished on a

vacuum line. The yield of the product ranged from 55 to 60%.

Other bis complexes containing mixed anions were prepared by mixing equimolar amounts (0.03 *M*) of $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ or $[\text{Cu}(\text{dach})_2](\text{NO}_3)_2$ dissolved in nitromethane with a nitromethane solution of the corresponding complex of the type $\text{Cu}(\text{dach})_2X_2$ where $X^- = \text{Cl}^-$, Br^- , or SCN^- . The two solutions were shaken on an automatic shaker for about 0.5 hr, and the solvent was removed under vacuum with a rotary evaporator. The compounds were dried on a vacuum line at 110°. The analytical data for these compounds are reported in Table I.

Attempts to synthesize complexes of nickel(II) containing two different kinds of anions were not successful. One perchlorate anion in $\text{Ni}(\text{dach})_2(\text{ClO}_4)_2$ could not be exchanged for either chloride or bromide.

Determination of Formation Constants.—The apparatus and method used in the determination of formation constants was described in a preceding paper in this series.¹²

Electrolytic Conductance Measurements.—Conductance measurements were made using a Wheatstone bridge consisting of a decade box resistor, an oscilloscope, and a sine-wave generator as a current source.^{17,18}

The conductivity cells were calibrated with 0.02 *N* potassium chloride prepared with conductivity water. The specific conductance of 0.02 *N* potassium chloride at 25° was taken as 0.002768 ohm⁻¹ cm⁻¹.¹⁹ For solutions of higher concentrations (10⁻³ *M*) a conductivity cell with "Platinized" platinum electrodes (15-mm diameter and 10 mm apart) of the general type explained by Shoemaker and Garland²⁰ was used whereas for solutions of lower concentrations (10⁻⁵ *M*), larger gold-plated electrodes (45-mm diameter and 5 mm apart) were used.¹⁹ The solutions of the complexes were made with doubly distilled practical grade nitromethane and the conductivity cells containing the solutions were equilibrated in a constant-temperature water bath for at least 15 min before the measurements were made. The resistance of the solutions was averaged from at least five readings from which the specific conductance was calculated. The observed conductivity was always corrected for the specific conductance of pure nitromethane. Replicate measurements were made on solutions of 10⁻³–10⁻⁵ *M* concentrations and values of molar conductance were plotted against \sqrt{C} to determine the effects of dilution (Figure 3 and Table IV).

Magnetic Susceptibility Measurements.—The magnetic moments of solid complexes were determined by the Gouy method at room temperature as described before¹² and are listed in Table V.

Spectral Measurements. Infrared Spectra.—The infrared absorption spectra of the solid complexes were obtained with either a Beckman IR-12 or a Beckman IR-8 infrared spectrophotometer. Some of the infrared spectra of the 1,5-diazacyclooctane complexes were obtained as potassium bromide pellets. Because of the possibilities of anion exchange in the 1,4-diazacycloheptane complexes, the infrared spectra were examined as Nujol or hexachlorobutadiene mulls instead of potassium bromide pellets.

Ultraviolet and Visible Absorption Spectra.—Visible and ultraviolet spectra of the complexes in different solutions were taken with a Cary Model 14 recording spectrophotometer using a set of matched 1-cm quartz cells. For the solvents where the solubility of a particular complex was low, a set of 5-cm matched quartz cells was used. The absorption spectra were always recorded using freshly prepared solutions, although all of the complexes were fairly stable in the nonaqueous solvents except formamide and pyridine. In aqueous solutions, the spectra of $\text{Cu}(\text{dach})_2^{2+}$ complexes were determined in the presence of excess

(14) M. S. Hussain and H. Hope, *Acta Cryst.*, in press. The crystal structure of $\text{Cu}(\text{dach})_2(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ has been determined by the three-dimensional X-ray method. The compound is monoclinic with space group $P2_1/n$ and the following cell parameters: $a = 20.924 \pm 0.016$ Å, $b = 15.794 \pm 0.016$ Å, $c = 10.040 \pm 0.010$ Å, $\beta = 91.68 \pm 0.033^\circ$, $V = 3316$ Å³, $D_c = 1.58$ g/cm³, $D_m = 1.60$ g/cm³ (floatation method) based on four formula units of $[\text{Cu}(\text{dach})_2(\text{NO}_3)] \cdot [\text{Cu}(\text{dach})_2\text{H}_2\text{O}](\text{NO}_3)_2$ per unit cell.

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(20) D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 196.

TABLE I
 ANALYTICAL DATA OF 1,4-DIAZACYCLOHEPTANE COMPLEXES

Complex	Color	Dec pt, °C	% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found
Mono-amine complex								
Cu(dach)Cl ₂	Light green	169	25.59	25.84	5.16	4.99	11.93	11.67
Bis-amine complexes								
Cu(dach) ₂ (ClO ₄) ₂	Maroon	237	25.95	25.77	5.21	5.29	12.11	11.97
Cu(dach) ₂ (NO ₃) ₂	Maroon	219	30.96	31.02	6.23	6.11	21.67	21.44
Cu(dach) ₂ Cl ₂	Purple	181	35.87	35.72	7.19	7.07	16.74	16.44
Cu(dach) ₂ Br ₂	Purple	187	28.35	28.47	5.69	5.55	13.23	13.03
[Cu(dach) ₂ Cl]ClO ₄ ^a	Blue	210	30.12	30.25	6.07	6.21	14.05	14.01
[Cu(dach) ₂ Br]ClO ₄ ^b	Blue	206	27.10	27.28	5.44	5.68	12.64	12.84
[Cu(dach) ₂ Cl]NO ₃	Blue	212	33.24	32.38	6.69	6.56	19.38	19.25
Ni(dach) ₂ (ClO ₄) ₂	Yellow	...	25.95	25.77	5.21	5.29	12.11	11.98
Ni(dach) ₂ Cl ₂	Yellow	...	36.39	35.27	7.30	7.29	16.98	17.05
Ni(dach) ₂ (NO ₃) ₂	Yellow	...	31.36	31.97	6.31	5.84	21.94	22.02

^a Perchlorate analysis: calcd, 24.94; found, 24.97. ^b Perchlorate analysis: calcd, 22.44; found, 22.79.

ligand. In methanol solvent, the solutions did not obey Beer's law and the maxima and intensities were not reproducible.

Reflectance Spectra.—The diffuse reflectance spectra of the complexes in the solid state were obtained with a standard Beckman DK-2 recording spectrophotometer equipped with a standard Beckman reflectance attachment using a magnesium oxide block as the reference. The visible spectra of the complexes in the solid phase were also obtained as Nujol mulls supported on filter paper as reported by Lee, Griswold, and Kleinberg.²¹

Results

The analytical data for the copper(II) and nickel(II) complexes of 1,4-diazacycloheptane, along with their decomposition points and color, are tabulated in Table I. The decomposition points of the nickel complexes are not reported. The melting point capillary containing bis(1,4-diazacycloheptane)nickel(II) perchlorate exploded when heated beyond 216° without any signs of melting or decomposition below this temperature. Owing to the explosive nature of the perchlorates the decomposition points were taken very carefully with extremely slow heating rates. All of the compounds are fairly stable to the atmosphere but long exposure to moisture has a profound effect on the elemental analyses.

The daco complexes of both nickel(II) and copper(II) are rather unreactive toward reagents which are known to cause decomposition of similar complexes.¹² For example, the addition of chloride, bromide, or cyanate ions to aqueous solutions of these complexes does not bring about noticeable color changes in the solution over long periods of time. Only slow discoloration is apparent when the nickel complex is treated with EDTA. However, the addition of cyanide discharges the color of both the nickel(II) and copper(II) complexes in a short time.

The yellow color of aqueous solutions of [Ni(dach)₂](ClO₄)₂ is discharged more easily by the addition of excess halides or EDTA than the corresponding solution of the daco complex. Likewise and in contrast to the daco complexes, the dach complexes of copper(II) are easily decomposed by 6 M hydrochloric acid. A

noticeable change in color also occurs on the addition of chloride, bromide, iodide, and thiocyanate ions to solutions of [Cu(dach)₂](ClO₄)₂ in noncoordinating solvents such as nitromethane, propylene carbonate, acetone, or acetonitrile. Dissociation of the perchlorate salt in coordinating solvents such as water, dimethyl sulfoxide, and formamide also causes an appreciable color change. However, the addition of halide ions to solutions of the complex in these polar solvents did not have any additional effect on the color of the solution.

To ascertain the possible coordination of the perchlorate and nitrate ions to the metal atom in the solid state, the infrared spectra of the solid complexes were analyzed as Nujol or hexachlorobutadiene mulls. The three infrared spectral bands at 1100–1130, 925, and 625 cm⁻¹, which were observed for perchlorate salts, are assigned to the T₂ (antisymmetric stretch), A₁ (symmetric breathing stretch), and T₂ (antisymmetric bend) absorptions of the perchlorate ion, respectively. The 625-cm⁻¹ band is a singlet and the 925-cm⁻¹ band is rather weak. Although the strong band near 1100 cm⁻¹ is sometimes a doublet, the fact that the 625-cm⁻¹ band is unsplit rules out any coordination of the perchlorate ion to nickel or copper.^{22,23} Whereas the infrared spectra of the perchlorate salts are strongly indicative of the T_d symmetry of the perchlorate ion, the infrared spectrum of Cu(dach)₂(NO₃)₂ is inconclusive for either D_{3h} or C_{2v} symmetry for the nitrate ion. The infrared spectra of Cu(dach)₂(NO₃)₂ in Nujol or hexachlorobutadiene mulls exhibited, in addition to the bands for uncoordinated nitrate ions,²⁴ a few weak absorptions which could be attributed to unidentate nitrate ions as shown by Gatehouse, Livingston, and Nyholm.²⁵ However, some of these bands were masked by the ligand absorption bands. The spectrum of Cu(dach)₂(NO₃)₂ is best explained if it is assumed that both uncoordinated (D_{3h}) and

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monodentate (C_{2v}) nitrate ions are present in the solid state. This conclusion was also inferred from the visible spectrum of the compound and was confirmed on the basis of a single-crystal X-ray analysis, which will be described shortly.¹⁴

The electronic absorption data of four-coordinated $Ni(daco)_2^{2+}$ and $Ni(dach)_2^{2+}$ complexes are presented in Table II along with the absorption maxima for two typical examples of square-planar nickel(II) complexes with intraligand π systems, $Ni(CN)_4^{2-}$ ²⁶ and $Ni[H_2B(pz)_2]_2$.²⁷ The bands which can be identified clearly as to energy and intensity are listed for the nickel complexes in different solvents. The nickel complexes of both 1,4-diazacycloheptane and 1,5-diazacyclooctane absorb near 440 $m\mu$ in the visible region in both the solid state and in solutions irrespective of the solvent and anion present. At this wavelength, the absorbance of a solution containing equivalent amounts of nickel(II) and ligand was exactly half that of a solution containing the same amount of nickel with 2 equiv of the diamine indicating that virtually all of the diamine was being used to form the bis-diamine complex and no

TABLE II
ELECTRONIC ABSORPTION SPECTRA OF
PLANAR NICKEL(II) COMPLEXES

Compound	Medium ^{a,b}	λ , $m\mu$	ν , cm^{-1}	ϵ , M^{-1} cm^{-1}	Assignment
$Ni(CN)_4^{2-}$ ^d	H_2O	445	(22,450)	2	$^1A_{1g} \rightarrow ^1A_{2g}$
		328	(30,500)	250	$^1A_{1g} \rightarrow ^1B_{1g}$
		310	32,300	700	$^1A_{1g} \rightarrow ^1E_g$
		284	35,200	4200	$^1A_{1g} \rightarrow ^1A_{2u}$
		266	37,600	10,600	$^1A_{1g} \rightarrow ^1E_u$
$Ni[H_2B(pz)_2]_2^e$	CH_2Cl_2	472	21,200	72	$^1A_{1g} \rightarrow ^1A_{2g}$
		277	36,100	1,400	$^1A_{1g} \rightarrow ^1B_{1u}$
		247	40,500	15,000	$^1A_{1g} \rightarrow ^1A_{2u}$
		242	41,300	21,000	$^1A_{1g} \rightarrow ^1E_u$
		234 ^c	42,700	15,000	$^1A_{1g} \rightarrow ^1E_u$
		219 ^c	45,700	12,000	Ligand
$[Ni(daco)_2](ClO_4)_2$	H_2O	445	22,450	115	$^1A_{1g} \rightarrow ^1A_{2g}$
		240	41,700	11,000	$^1A_{1g} \rightarrow ^1A_{2u}$
		(220)	(45,450)	8200	$^1A_{1g} \rightarrow ^1E_u$
		205	48,800	9900	$^1A_{1g} \rightarrow ^1E_u$
		445	22,450	112	$^1A_{1g} \rightarrow ^1A_{2g}$
$[Ni(dach)_2](ClO_4)_2$	H_2O	445	22,450	...	$^1A_{1g} \rightarrow ^1A_{2g}$
		425	23,550	85	$^1A_{1g} \rightarrow ^1A_{2g}$
		425	23,550	100	$^1A_{1g} \rightarrow ^1A_{2g}$
		420	23,400	...	$^1A_{1g} \rightarrow ^1A_{2g}$
$[Ni(dach)_2](NO_3)_2$	CH_3NO_2	425	23,550	100	$^1A_{1g} \rightarrow ^1A_{2g}$
		Solid	415	24,100	...

^a In the solid state and in the nitromethane solutions, only the maxima observed in the visible region are listed. ^b Poorly resolved peaks and shoulders are enclosed in parentheses. ^c Cyclohexane solution. ^d H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963). ^e J. D. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3148 (1967). $H_2B(pz)_2$ = bis(1-pyrazolyl) borate.

mono complex was present. A continuous-variation study of the nickel(II)-dach complexes further confirmed that the complex in solution was $Ni(dach)_2^{2+}$. Similar studies with copper(II) revealed that both mono and bis complexes were formed and each could be isolated in analytically pure form.

The electronic absorption spectra of the four-coordinated copper complexes are reported in Table III.

It is interesting to note that the first d-d transition in the $[Cu(daco)_2](ClO_4)_2$ complex occurs at about 500 $m\mu$ (19,950 cm^{-1}), whereas the corresponding values in related, presumably four-coordinated, planar complexes are around 540 $m\mu$ (18,450 cm^{-1}). Only in the solid state and in solvents of very low coordinating capacity did the visible absorption band for the $[Cu(dach)_2](ClO_4)_2$ reach the value of λ_{max} observed for the solid $[Cu(daco)_2](ClO_4)_2$ suggesting that the solvent may be involved in coordination to the metal. For example, in nitromethane the λ_{max} of $Cu(dach)_2^{2+}$ is 505 $m\mu$, whereas in water the λ_{max} is 542 $m\mu$.

Since the λ_{max} values for the nitromethane solutions and for the reflectance spectra were identical and the spectral contours were very similar, it is assumed that the structure of $[Cu(dach)_2](ClO_4)_2$ in nitromethane is similar to the structure in the solid state. However, the color of the nitromethane solutions (Figure 1) of $Cu(dach)_2^{2+}$ was found to vary with the anion present. While the λ_{max} value of a d-d transition in the visible region of the spectrum of $[Cu(dach)_2](ClO_4)_2$ was 505 $m\mu$, the absorption occurred at much higher wavelengths (610 $m\mu$) for copper complexes containing other anions (e.g., Cl^- , Br^- , SCN^- , I^- , etc.). Anion coordination is also important in other solvents having low dielectric constants such as methanol ($D_{25^\circ} = 32.6$) and acetone ($D_{25^\circ} = 20.7$). The visible absorption spectra of the dach complexes containing various anions in several solvents for the spectral range 360–950 $m\mu$, along with the diffuse reflectance spectra for the region 350–850 $m\mu$, are also given in Table III. However, the spectra of the complexes become completely independent of the anions in solvents of high dielectric constant such as water ($D_{25^\circ} = 78.5$) and formamide ($D_{25^\circ} = 109$). Dach complexes are unstable in formamide. The band in the visible region is shifted to higher wavelengths on standing, but the spectra of the aqueous solutions remain unchanged for several days in the presence of excess ligand.

That these halodiamine complexes in noncoordinating solvents contain five-coordinated copper is indicated by a spectrophotometric titration of the four-coordinate perchlorate salt with halide ions in nitromethane. A single isosbestic point at 544 $m\mu$ (18,350 cm^{-1}) is observed when bis(1,4-diazacycloheptane)copper(II) perchlorate is titrated with either tetraethylammonium chloride or bromide up to a 1:1 complex:halide ratio (Figure 2). The spectrum of the resulting solution was similar to that observed by mixing $[Cu(dach)_2](ClO_4)_2$ with $[Cu(dach)_2Cl]Cl$ or $[Cu(dach)_2Br]Br$ in equimolar proportions. Both spectra were identical with the spectra of analytically pure $[Cu(dach)_2Cl]ClO_4$ or $[Cu(dach)_2Br]ClO_4$ synthesized by the exchange of one perchlorate ion from $[Cu(dach)_2](ClO_4)_2$ with lithium chloride or lithium bromide.

The single isosbestic point can be envisioned as evidence for the presence of both four- and five-coordinated species in the solution. Similar spectrophotometric titrations of bis(1,4-diazacycloheptane)-copper(II) nitrate also showed a single isosbestic point.

(26) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(27) J. D. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3148 (1967).

TABLE III
 ELECTRONIC ABSORPTION SPECTRA OF COPPER(II) COMPLEXES

Compound	Medium	λ , m μ	ν , cm $^{-1}$	ϵ , ^b M $^{-1}$ cm $^{-1}$	Comments ^c
[Cu(daco) ₂](ClO ₄) ₂	Solid	500	20,000	...	d-d, P
	CH ₃ NO ₂	495	20,300	340	d-d, P
	H ₂ O	500	20,000	295	d-d, P
		278	34,500	4600	L-M
		(240)	(40,800)	3000	L-M
	CH ₃ CN	505	19,800	304	d-d, P
		300	33,350	5900	L-M
		CH ₃ OH	500	20,000	300
	(360)		27,800	1100	
	300		33,350	5000	L-M
	255 sh		39,200	4100	L-M
[Cu(dach) ₂](ClO ₄) ₂	Solid	495	20,300	...	d-d, P
	CH ₃ NO ₂	505	19,800	172	d-d, P
	H ₂ O	542	18,450	134	d-d, SP
		261	38,200	4000	L-M
	CH ₃ OH	532	18,800	240	d-d, SP
[Cu(dach) ₂ Cl]ClO ₄	Solid	580	17,200	...	d-d, SP
	CH ₃ NO ₂	615	16,200	209	d-d, SP
	H ₂ O	542	18,500	121	d-d, SP
		260	38,450	4250	
[Cu(dach) ₂ Br]ClO ₄	Solid	580	17,300	...	d-d, SP
	CH ₃ NO ₂	610	16,400	224	d-d, SP
	H ₂ O	542	18,500	121	d-d, SP
		260	38,450	4350	
[Cu(dach) ₂ Br]Br	Solid	600	16,700	...	d-d, SP
	CH ₃ NO ₂	610	16,500	214	d-d, SP
	Water	542	18,500	123	d-d, SP
		250	38,450	4250	
	CH ₃ OH	590	16,950	143	d-d, SP
[Cu(dach) ₂ Cl]Cl	Solid	585	16,250	...	
	CH ₃ NO ₂	610	16,300	213	d-d, SP
	H ₂ O	542	18,500	131	d-d, SP
		260	38,450	4300	
	CH ₃ OH	590	16,950	224	d-d, SP
[Cu(dach) ₂ NO ₃](NO ₃)	Solid	530	18,850	...	d-d, SP
	CH ₃ NO ₂	535	18,700	180	d-d, SP
	H ₂ O	542	18,500	131	d-d, SP
		260	38,450	4300	
	CH ₃ OH	550	18,000	135	d-d, SP
[Cu(trenMe)Br]Br ^{a,d}	Solid	1000	10,000	...	TB
		781	12,800	...	
		(370)	(27,000)	...	
	CHCl ₃	962	10,400	450	
		752	13,300	209	
[Cu(trenMe)NO ₃](NO ₃) ^{a,d}	Solid	901	11,100	...	TB
		(725)	(13,800)	...	
	C ₂ H ₅ NO ₂	893	11,200	445	
		(699)	(14,300)	...	
	375	26,700	386		

^a trenMe = tris(2-dimethylaminoethyl)amine, N[CH₂CH₂N(CH₃)₂]₃. ^b The values of the extinction coefficients for the high-intensity bands in the ultraviolet region are to be considered accurate to the order of magnitude. ^c Abbreviations: d-d, d-d transition; L-M, ligand-to-metal transition; P, planar; SP, square pyramidal; TB, trigonal bipyramidal. ^d M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

As expected, this behavior is in marked contrast to the spectral behavior of the diperchlorate or dinitrate salts of Cu(daco)₂²⁺ where the addition of halide resulted in a negligible spectral change. The only effect which was noted was that the peak at 500 m μ became somewhat less intense after standing for more than 2 hr.

One of the methods of synthesizing compounds containing mixed anions involved the shaking of equimolar amounts of the diperchlorate salts with the dihalides in nitromethane. For example, the mixing of a 1:1 molar ratio of the [Cu(dach)₂](ClO₄)₂ and Cu-

(dach)₂Br₂ complexes results in 2 mol of [Cu(dach)₂-Br]ClO₄. To substantiate the formation of the mixed anion complex, the spectrum of the resulting solution was not observed as a simple addition of the spectra of the starting materials, but rather it was identical with the spectrum of [Cu(dach)₂Br]ClO₄ obtained by exchange of one perchlorate ion with lithium bromide.

Interestingly, when equimolar amounts of Cu(dach)₂(NO₃)₂ and [Cu(dach)₂](ClO₄)₂ were mixed, the spectrum of the resulting solution suggested the formation of a new species, with a λ_{max} at 535 m μ which can be

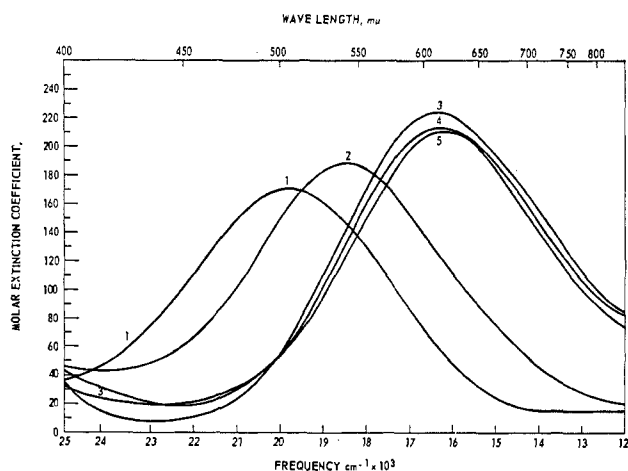


Figure 1.—Visible absorption spectra of bis(1,4-diazacycloheptane)copper(II) complexes in nitromethane: (1) $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$; (2) $[\text{Cu}(\text{dach})_2\text{NO}_3]\text{NO}_3$; (3) $[\text{Cu}(\text{dach})_2\text{Br}]\text{ClO}_4$; (4) $\text{Cu}(\text{dach})_2\text{Cl}_2$; (5) $[\text{Cu}(\text{dach})_2\text{Cl}]\text{ClO}_4$.

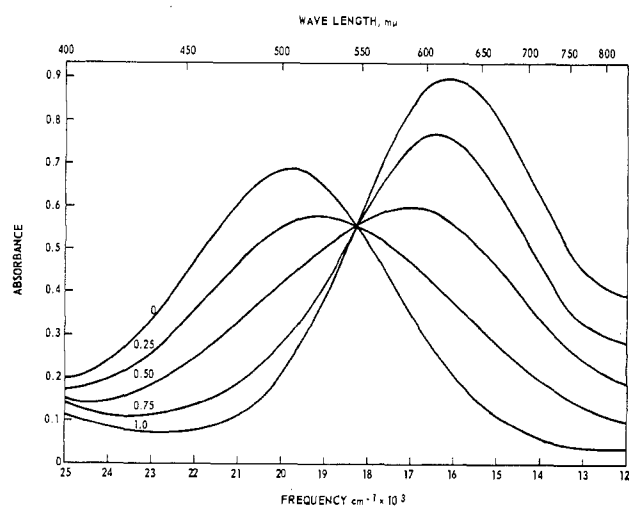


Figure 2.—Visible absorption spectra of various mixtures of $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ and $(\text{C}_2\text{H}_5)_4\text{NCl}$ in nitromethane. The numbers represent the $\text{Cl}^-:\text{Cu}(\text{dach})_2^{2+}$ molar ratio.

formulated as $[\text{Cu}(\text{dach})_2\text{NO}_3]\text{ClO}_4$. Since the $[\text{Cu}(\text{dach})_2\text{NO}_3]\text{ClO}_4$ complex was not synthesized by an independent route, the compound was characterized by noting that the absorbance of the solution could be predicted by assuming that the principal absorbing species is the $\text{Cu}(\text{dach})_2\text{NO}_3^+$ cation. The extinction coefficient of the species had already been determined by analysis of the $\text{Cu}(\text{dach})_2(\text{NO}_3)_2$ complex.

Although a differentiation between nitrate and perchlorate interaction with a metal has often been observed in the solid state, in this case we could observe differences between perchlorate and nitrate coordination to a metal ion in solution.²⁸

During the spectrophotometric titrations of $\text{Cu}(\text{dach})_2^{2+}$ with halides, slight changes in the spectra were observed and the spectrum contours no longer showed the isosbestic point at $544 \text{ m}\mu$ when the halide concentrations were increased above a 1:1 ratio. The

spectral changes, however, were so slight ($5\text{-m}\mu$ shift in λ_{max} with a 4:1 excess of halide present) that coordination on the sixth site cannot be readily invoked to explain the perturbation. The spectra of 10^{-3} M solutions of $\text{Cu}(\text{dach})_2\text{Br}_2$ and $\text{Cu}(\text{dach})_2\text{Cl}_2$ in nitromethane are very similar to those of $[\text{Cu}(\text{dach})_2\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{dach})_2\text{Cl}]\text{ClO}_4$, respectively. This observation strongly suggests that the dihalides should also be included in the series of five-coordinated complexes and should be formulated as $[\text{Cu}(\text{dach})_2\text{Br}]\text{Br}$ and $[\text{Cu}(\text{dach})_2\text{Cl}]\text{Cl}$. Contrary to the spectral observations, conductance data in nitromethane show that the dihalide salts are only weakly conducting. However, on dilution the curves can be extrapolated to approach the curves of a 1:1 electrolyte (Figure 3). This behavior points either to a strong association of the complex in nitromethane or to the formation of an octahedral species which breaks down on dilution. The latter is less probable, because coordination at the sixth position should be reflected by a marked variation in the spectral properties of the molecule. Some ionic association also may be occurring in solutions of the other complexes in nitromethane, Table IV, since the conductivity is slightly lower than expected and on dilution a pronounced increase in conductivity is always observed.

The magnetic susceptibilities of all of the crystalline 1,5-diazacyclooctane and 1,4-diazacycloheptane compounds reported were measured at room temperature on several different samples. The mean values of the corrected molar magnetic susceptibilities and the values of the diamagnetic corrections calculated from Pascal's constants are presented in Table V. Corrections for temperature-independent paramagnetism and possible non-Curie-law behavior were not considered.

The $\text{p}K_A$'s of *daco* and *dach* have already been reported^{12,29} along with the formation constants for *daco* complexes of nickel(II) and copper(II).¹² The

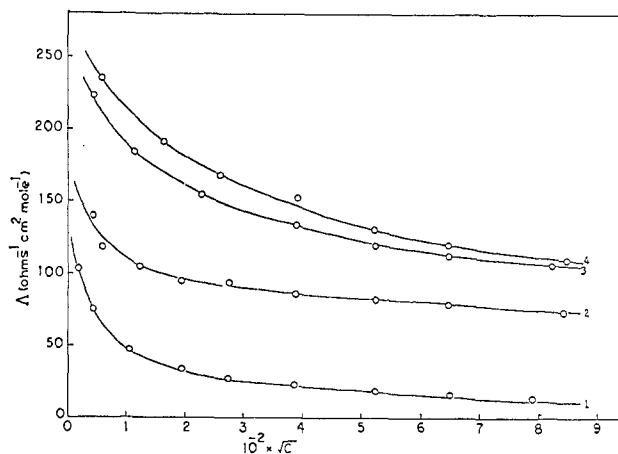


Figure 3.—Molar conductance in nitromethane at 25° : (1) $\text{Cu}(\text{dach})_2\text{Cl}_2$; (2) $[\text{Cu}(\text{dach})_2\text{Cl}]\text{ClO}_4$; (3) $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$; (4) $[\text{Cu}(\text{daco})_2](\text{ClO}_4)_2$.

TABLE IV
MOLAR CONDUCTANCE OF COPPER(II) AND NICKEL(II)
COMPLEXES IN NITROMETHANE AT 25°

Complex	Concn, <i>M</i>	Molar conductance, cm ² ohm ⁻¹ mol ⁻¹	Ref
Weak electrolytes			
Cu(dienMe)Cl ₂	10 ⁻³	16.1	<i>b</i>
Cu(dach) ₂ Cl ₂	3 × 10 ⁻³	16	...
Cu(dach) ₂ Br ₂	3 × 10 ⁻³	19	...
Uni-univalent electrolytes			
[Cu(Mepic) ₂ Cl]ClO ₄	10 ⁻³	98.8	<i>c</i>
[Cu(trenMe)Br]Br ^a	10 ⁻³	79	<i>d</i>
[(<i>n</i> -C ₄ H ₉) ₄ N]Br ^a	10 ⁻³	70	<i>d</i>
[Cu(dach) ₂ Cl]ClO ₄	3 × 10 ⁻³	82	...
[Cu(dach) ₂ Br]ClO ₄	3 × 10 ⁻³	79	...
[Cu(dach) ₂ NO ₃]NO ₃	3 × 10 ⁻³	83	...
Uni-bivalent electrolytes			
[Cu(Mepic) ₂](ClO ₄) ₂	10 ⁻³	152	<i>c</i>
[Ni(detu) ₂](ClO ₄) ₂ ^a	1.5 × 10 ⁻⁴	138	<i>e</i>
[Cu(dach) ₂](ClO ₄) ₂	1.5 × 10 ⁻³	134	...
	3.0 × 10 ⁻³	113	...
[Cu(daco) ₂](ClO ₄) ₂	3.0 × 10 ⁻³	132	...
[Ni(dach) ₂](ClO ₄) ₂	3.0 × 10 ⁻³	146	...
[Ni(dach) ₂]Cl ₂	3.0 × 10 ⁻³	123	...
[Ni(daco) ₂](ClO ₄) ₂	4.0 × 10 ⁻³	138	...

^a The molar conductivity reported in nitroethane. ^b M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966). ^c S. Utsumo and K. Sone, *J. Inorg. Nucl. Chem.*, **28**, 2647 (1966). ^d M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966). ^e S. L. Holt, Jr., and R. L. Carlin, *J. Am. Chem. Soc.*, **86**, 3017 (1964).

TABLE V
MAGNETIC PROPERTIES OF SOLID COPPER(II) AND NICKEL(II)
COMPLEXES OF CYCLIC DIAMINES AT ROOM TEMPERATURE

Compound	Temp, °K	Diamag cor × 10 ⁻⁶	Cor 10 ⁻⁶ XM, cgsu	μ_{eff} , BM
[Cu(dach) ₂](ClO ₄) ₂	294	217	1544	1.92
[Cu(dach) ₂ NO ₃]NO ₃	294	190	1553	1.92
[Cu(dach) ₂ Cl]Cl	295	199	1587	1.94
[Cu(dach) ₂ Br]Br	294	222	1553	1.92
[Cu(dach) ₂ Cl]ClO ₄	294	221	1405	1.82
[Cu(dach) ₂ Br]ClO ₄	294	219	1426	1.83
[Ni(dach) ₂](ClO ₄) ₂	295	217	103	0.41

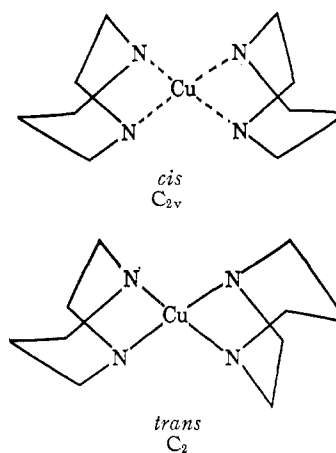
formation constants for the dach complex of copper were reported²⁹ and subsequently confirmed in this work ($\log K_1^{25^\circ} = 7.61 \pm 0.05$; $\log K_2^{25^\circ} = 6.21 \pm 0.04$). The over-all formation constant for the dach complex of nickel was determined ($\log K_T^{25^\circ} = 8.31 \pm 0.2$). No evidence for a 1:1 complex was observed so the stepwise constants are not reported. The value of the over-all formation constant for Ni(dach)₂²⁺ is in marked contrast to the value of the Ni(daco)₂²⁺ complex ($\log K_T^{25^\circ} = 18.68 \pm 0.12$). This difference may be accounted for by considering the more extensive solvation of the dach complexes in water which reduces the strength of the metal-nitrogen interaction and increases the specific interaction of solvent with the metal. When these effects are compared with the daco complex where solvent effects at the metal atoms are minimal and the full inductive effect of the secondary amine can be felt at the metal atom, the decreased stability constant is not unexpected.

Discussion

Molecular models indicate that a nearly square and

perfectly planar arrangement of four nitrogen atoms (local symmetry *D*_{4h}) would be present when two daco or dach molecules are chelated to a metal ion. In the daco complexes each of the cyclic ligands can be arranged in a twisted crown, a saddle, or a boat-chair configuration. However, the boat-chair conformation for both ligands was suggested¹² in order to minimize all nonbonded interactions. In this conformation, the axial positions of the metal ion are effectively shielded and additional coordination is prohibited. This conformation adequately accounts for the insensitivity of the visible absorption maxima and magnetic properties of the complex to changes in the anion and the solvent.

In contrast to the symmetrical disposition of daco molecules around the metal ion, it is possible for two 1,4-diazacycloheptane rings to coordinate to the central metal ion in two different ways. The two-carbon chains can be on the same side of the plane (*cis*) formed by the four nitrogen atoms or they may be on opposite sides of the plane (*trans*). The *cis* configuration with each ring in the double boat form has been shown to be the correct configuration in



the pyramidal molecule Cu(dach)₂(NO₃)₂·0.5H₂O, by crystal structure analysis,¹⁴ and this configuration is presumed to exist in the other dach complexes.

This assumption will not cause us any difficulty in discussing the properties of the planar complexes which occur when noncoordinating solvents and anions are present since only the four planar nitrogen atoms will exert a major influence on the metal atoms with the carbon chains playing a passive role. However, in the presence of coordinating solvents and anions the *cis* form can easily accommodate a fifth ligand proximate to the metal to give a pyramidal structure whereas the *trans* form would have the potential to coordinate with two additional ligands to give a tetragonally distorted octahedral structure. Thus, it is probable that under certain conditions an equilibrium between the *cis* and *trans* forms of the diamine complex may exist and perhaps in certain complexes the *trans* form may predominate. Since we know that the *cis* form is present in the pyramidal complex, but no evidence is currently available for the existence of a *trans* form,

we have attempted to account for all of the properties of these complexes by assuming that only the *cis* form is present and that each *dach* ligand is in the double-boat configuration. Perhaps deviations from the expected behavior may then be rationalized in terms of the *trans* form.

Nickel Complexes.—In the solid state at room temperature all of the yellow $\text{Ni}(\text{dach})_2^{2+}$ complexes are diamagnetic and a planar coordination geometry is indicated. The spectral properties of the nickel complex are essentially invariant between the solid and solution suggesting that the planar geometry is retained. However, in good coordinating solvents the yellow color slowly disappears indicating that a slow decomposition is occurring.

Gray and Ballhausen²⁶ have discussed molecular energy level schemes for square-planar metal (d^8) complexes in which the ligands themselves have no π -orbital system (Cl^- , Br^- , H_2O^- , NH_3) and for complexes in which the ligands have a π system (CN^-), with particular emphasis on the assignments of the charge-transfer bands observed in such complexes. In the former case, which applies to these medium-ring complexes, three spin-allowed $d-d$ type transitions were suggested. All of these are parity forbidden as electronic dipole transitions. In addition to these transitions, two allowed charge-transfer transitions are also suggested. The charge-transfer transitions must arise from molecular orbitals essentially localized on the ligands to molecular orbitals essentially localized on the metal atom.²⁶

Three distinct maxima from 195 to 950 $m\mu$ were observed for $[\text{Ni}(\text{daco})_2](\text{ClO}_4)_2$ in water. These bands are in the regions 210–220, 235–245, and 440–450 $m\mu$. Similar absorption spectra were observed for $[\text{Ni}(\text{daco})_2](\text{ClO}_4)_2$ in methanol and acetonitrile solvents except for certain peaks in the ultraviolet region which were obscured by absorption bands of acetonitrile. The band at 445 $m\mu$ must be assigned to the first $d-d$ transition in view of its extinction coefficient. The band is somewhat more intense than the corresponding transition in the compounds studied by Gray and Ballhausen²⁶ and by Jesson, Trofimenko, and Eaton.²⁷ However, the band is symmetrical, and a search at longer wavelengths with more concentrated solutions did not reveal any further absorptions. The first charge-transfer transition can be assigned to the band at 240 $m\mu$ with a high extinction coefficient.

Because of the separation of the $^1A_{1g} \rightarrow ^1A_{2g}$ band at 440 $m\mu$ and the tail of the charge-transfer band at 330 $m\mu$, we expected that the $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_g$ transitions would have been observable if they were present in this region.²⁹ However, no significant absorption was observed in rigorously purified samples. To escape detection these bands must either be very weak or buried under other absorptions.

We hoped that an analysis of the charge-transfer bands for the nickel(II) complexes would offer a clarification of the planar structure. From a comparison of the spectra of planar d^8 complexes where the ligand

has no π system with those cases where a π system is present, Gray and Ballhausen²⁶ concluded that for ligand-to-metal transitions (exhibited unambiguously by complexes without an intraligand π system) the two charge-transfer bands are separated by nearly 10,000 cm^{-1} , whereas for metal-to-ligand transitions (shown by complexes with an intraligand π system), the three charge-transfer bands are more closely spaced (approximately 2000–3000 cm^{-1} apart).

A separation of 2000–3000 cm^{-1} was observed for the three charge-transfer bands in $\text{Ni}(\text{CN})_4^{2-}$ ²⁶ and $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$.²⁷ In these complexes an intraligand π system is present and the transitions were assigned to metal-to-ligand transitions. However, three intense bands are also present in the ultraviolet region of $[\text{Ni}(\text{daco})_2](\text{ClO}_4)_2$ in water. The separation of the maxima at 42,000 and 49,000 cm^{-1} would conform to the expected splitting pattern of the two charge-transfer bands but then the shoulder at 45,500 cm^{-1} seems to be anomalous.

We attempted to observe ultraviolet spectra of other $\text{Ni}(\text{dach})_2^{2+}$ complexes but were unable to obtain accurate absorbance readings owing to the slow solvolysis of the complex. In $[\text{Ni}(\text{dach})_2]\text{Cl}_2$ in methanol only a single intense band ($\epsilon \sim 8000$) appears at $\sim 240 m\mu$ whereas in $[\text{Ni}(\text{dach})_2](\text{NO}_3)_2$ the only observable band is near 200 $m\mu$.

The $\text{Ni}(\text{daco})_2^{2+}$ cation is almost as inert to ligand substitution and decomposition as the nickel complexes of maleonitriledithiolate, $\text{Ni}(\text{MNT})_2^{2-}$.³⁰ In the MNT complexes it was argued that the unreactivity was due to an interaction between the p_z orbital on the metal and the extensive π -orbital system of the ligands. This π interaction would overcome any extra stability which might be gained by forming additional σ bonds with axial groups. In the *daco* complexes steric shielding of the z axis adequately accounts for the unreactivity. The $\text{Ni}(\text{dach})_2^{2+}$ complexes are rather unreactive, but since $\text{Cu}(\text{dach})_2^{2+}$ easily accommodates a fifth ligand in the coordination sphere, a simple steric effect cannot be invoked to account for the unreactivity. A possible explanation may be that the strong field induced in the $X-Y$ plane by the ligand prevents incoming axial ligands from effectively interacting with the filled d_{z^2} orbital. However, interactions involving the metal p_z orbital may provide a route for decomposition and, in addition, may be responsible for some of the transitions observed in the ultraviolet region which have not been assigned.

Copper Complexes.—An examination of the visible absorption spectra of $\text{Cu}(\text{daco})_2^{2+}$ and $\text{Cu}(\text{dach})_2^{2+}$ complexes is probably the best method for studying the coordination of copper. The spectra of $[\text{Cu}(\text{daco})_2](\text{ClO}_4)_2$ in water and methanol are similar. The bands in the regions 240–255 and 280–300 $m\mu$ can be assigned to two ligand-to-metal charge-transfer bands and the and at 500–510 $m\mu$ can be assigned to the forbidden crystal field transitions between the 3d levels. Owing

to the symmetry of the band at 500 $m\mu$ at room temperature it is impossible to separate out the individual d-d transitions. The visible spectrum of this complex in the weakly coordinating solvent nitromethane also showed a maximum at 500 $m\mu$ but the ultraviolet region was not observable owing to the absorption of the solvent.

In contrast to the insensitivity of $[\text{Cu}(\text{daco})_2](\text{ClO}_4)_2$ to solvent due to the effective screening of the metal ion by the hydrocarbon chain, the spectrum of $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ is markedly solvent dependent. The solid $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ is a light red solid (λ_{max} 495 $m\mu$) which dissolves in nitromethane to give a maroon solution with an absorption maximum at 505 $m\mu$. Since the maximum in solution is similar to that in the solid and is identical with that observed for the daco complex in the solid and in solution, it can be assumed that the environment around the copper ion in $\text{Cu}(\text{dach})_2^{2+}$ is planar and neither the solvent nor the anion is strongly coordinated. Then, if the absorption maximum of $\text{Cu}(\text{dach})_2^{2+}$ in nitromethane is taken as a standard (505 $m\mu$), a significant shift toward lower energy (longer wavelengths) is observed with solvents which are known to be good nucleophiles. The shifts relative to nitromethane are as follows: formamide, +40 $m\mu$; water, +37 $m\mu$; dimethyl sulfoxide, +30 $m\mu$; methanol, +25 $m\mu$; acetonitrile, +20 $m\mu$; and acetone, +5 $m\mu$. In a related planar copper complex, bis(salicylaldehydeethylenediimine)copper(II), the position of the maximum is observed at 562 $m\mu$ in noncoordinating solvents and the maximum also moves to longer wavelength in the presence of coordinating solvents.^{31,32} In this complex it was postulated that the shift to lower energy was indicative of the formation of a pentacoordinated complex. Although the maxima observed in these medium-ring diamine complexes are lower than those observed in the salicylaldehyde imine complex for similar geometric structures, the shift is in the same direction and the difference may be attributable to effects of the π system.

On the basis of the variation of the visible spectra of $\text{Cu}(\text{dach})_2^{2+}$ upon the addition of coordinating solvents, it can be concluded that the solvent becomes intimately involved in the coordination sphere of the metal as long as a minimum nucleophilicity and steric requirement are fulfilled. As expected, when well coordinating anions are added to a solution of $\text{Cu}(\text{dach})_2^{2+}$ dissolved in nitromethane, coordination occurs, and a pentacoordinated complex is obtained having a λ_{max} at 610 $m\mu$.

In strongly coordinating solvents such as water and formamide the spectra are independent of the anion present and solutions of all of the salts absorbed at 542 $m\mu$. It is worth noting that on solution in coordinating solvents, the maximum for pyramidal complexes with an anion in the apical position is shifted to higher energy (610 \rightarrow 542 $m\mu$), whereas the maximum observed for the planar complex is shifted to lower

energy (500 \rightarrow 542 $m\mu$). This effect can be attributed to a solvolysis of the pentacoordinated complex in which the coordinated anion is replaced by a solvent molecule. In the planar complex a simple addition of a solvent molecule along the C_2 axis gives the same product. It appears that a water molecule and a nitrate ion have a similar coordinating ability since $\text{Cu}(\text{dach})_2\text{NO}_3^+$ and $\text{Cu}(\text{dach})_2\text{H}_2\text{O}^{2+}$ absorb in the same region of the spectra. That these two ions have identical structures was shown¹⁴ by a crystal structure analysis of $[\text{Cu}(\text{dach})_2](\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ where two structurally different copper atoms are present in the unit cell. One of the copper atoms is surrounded by a planar array of four nitrogen atoms with a nitrate ion in the apical position whereas the other copper atom has a water molecule in the apical position. The most important point to emphasize about the two ions is that *all* of the internuclear distances are almost identical regardless of whether the neutral water molecule or the negative nitrate ion occupies the fifth position.¹⁴

To correlate the position of the maximum in the visible absorption spectrum of $\text{Cu}(\text{dach})_2^{2+}$ complexes with various nucleophiles in the fifth position, the following order may be given showing the decreasing effect on the planar copper ion: $\text{Cl}^- \sim \text{Br}^- \sim \text{SCN}^- > \text{HCONH}_2 > \text{H}_2\text{O} > \text{NO}_3^- \sim \text{DMSO} > \text{CH}_3\text{OH} > \text{CH}_3\text{CN} > (\text{CH}_3)_2\text{CO} > \text{CH}_3\text{NO}_2 \sim \text{ClO}_4^-$.

We attempted to examine the ultraviolet spectra of $\text{Cu}(\text{dach})_2^{2+}$ complexes in water and in methanol; however, the solutions of the complexes in these solvents did not obey Beer's law on dilution even in the presence of excess ligand. Thus, the spectra are difficult to reproduce and the maxima in the ultraviolet spectra cannot be unambiguously assigned to specific species in solution.

It is useful to compare the properties of square-pyramidal and trigonal-bipyramidal complexes of copper where the molecule is of the type MN_4X^+ and none of the ligands has a π system. The $\text{Cu}(\text{dach})_2\text{X}^+$ and the tris(2-dimethylaminoethyl)amine complex $[\text{Cu}(\text{trenMe})\text{X}^+]$ systems satisfy this requirement. Although no complexes with mixed anions are known for trenMe, the reflectance spectra of the dibromide and diperchlorate salts of $\text{Cu}(\text{trenMe})\text{X}^+$ ³¹ show multiple absorption maxima at generally lower energies (10,000, 12,800, and 27,000 cm^{-1} and 11,300 and 13,500 cm^{-1}) than the $\text{Cu}(\text{dach})_2^{2+}$ complexes with the same anions. Perhaps the best comparison can be made with $[\text{Cu}(\text{trenMe})\text{NO}_3]\text{NO}_3$ which absorbs at 11,100 and 13,800 cm^{-1} in the solid state and at 11,200, 14,300 sh, and 26,700 cm^{-1} in nitroethane. Thus a simple examination of the spectral properties of related pentacoordinated complexes can easily be used to distinguish between the two different geometric structures.

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