spectrum cannot be used to differentiate between geometrical isomers. However, some useful information concerning the geometry of the Co(III) complexes has been derived from the resonances in the $-CH_3$ and $=CH-$ regions. First the $-CH_3$ and $=CH-$ resonances occur as sharp singlets, even when the nmr spectrum is expanded. Since the pure *uns-cis*-[Co(BTAT)]$^+$ isomer contains two sets of nonequivalent methyl and methine protons, the nmr spectrum of this isomer, barring any accidental degeneracies, should exhibit two singlets in the methyl and methine regions, respectively. To rule out the possibility of accidental degeneracy, the ^{19}F nmr spectrum of [Co(BTAT)]Br in methanol has been obtained. A slightly broad, symmetrical singlet due to the $-CF_3$ resonance was observed at -72.4 ppm. Therefore, since only one methyl and CF_3 resonance was observed in the ^1H and ^{19}F nmr spectrum, the possibility that [Co(BTAT)]Br exists solely as the uns-cis isomer can be eliminated. This is supported by the interpretation of the electronic spectra (*vide infra*). A similar line of reasoning has been used to eliminate the possibility of there being a mixture of isomers present, since the chemical shifts of the $-CH_3$ and $=CH-$ protons should differ for each isomer. Therefore, the formation of the complex must proceed stereospecifically to yield only one of the four possible isomers. While it is impossible to distinguish between pure forms of the two s-cis isomers and the trans isomers by physical measurements other than X-ray diffraction, considerations of stereomodels of these Co(III) complexes and the corresponding Ni(II) and Cd(II) complexes show that structures V–VII are greatly strained at the imine nitrogen which leaves structure IV as the only possible isomer. This preference for formation of complexes of s-cis geometry has been well documented for other Co(III) and Ni(II) complexes.[23-27] In view of the preceding discussion it has been concluded that syntheses of Co(BTAT)X, Ni(BTAT), Ni(BHAT), and Cd(BTAT) proceed stereospecifically with formation of only the s-cis isomer.

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A New Ring-Opening Reaction of Aziridines in Nickel(II) and Copper(II) Complexes

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Reaction of the bis-salicylaldehydo complexes of nickel(II) and copper(II) with *N*-(2-aminoethyl)aziridine, AEA, and *N*-(3-aminopropyl)aziridine, APA, gives neutral complexes of the expected Schiff base condensation products, salAEA and salAPA, respectively. These complexes are characterized by their analyses, vibrational and electronic spectra, molecular weights, and magnetic moments. The reaction of nickel(II) acetate and copper(II) acetate with salicylaldehyde and AEA results in the formation of bis(salicylidene)ethylenediiminenickel(II) and bis(salicylidene)ethylenediiminecopper(II), respectively. In the presence of acetic acid, the neutral complex Ni(salAEA)$_2$ reacts to give bis(salicylidene)ethylenediiminenickel(II). These reactions represent a new type of ring-opening reaction of aziridine.

Introduction

In the course of a study of the complexes formed by aziridines[1] and *N*-(aminoalkyl)aziridines,[2] we have investigated complexes of the Schiff bases derived from reactions of salicylaldehyde with *N*-(2-aminoethyl)aziridine, AEA, and *N*-(3-aminopropyl)aziridine, APA.[3] The salicylidene Schiff bases of unsymmetrically N-substituted diamines have been studied extensively as ligands.[4-13] This work is the first report in which the third donor atom of a potentially tridentate salicylaldimine ligand is the nitrogen of an aziridine ring. Furthermore, a unique ring-opening reaction has been discovered in which both carbon–nitrogen bonds are cleaved under mild conditions in the presence of nickel(II) and copper(II).

The aziridine ring is well known as an alkylating agent, mutagen, antimicrobial and sterilant, and the sizable literature on aziridine chemistry has been reviewed thoroughly by Dermer and Ham.[14] The use of metal ions in facilitating ring-opening reactions of aziridine has been explored with Al(III)[15] and iron(III)[16]

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but these reactions have not been studied in detail. If ring opening is involved in the biological activity of an aziridine-ring-containing compound, coordination of the ring through its nitrogen atom is likely to alter the activity.

In this paper we shall report two strikingly different reactions which take place when Schiff bases derived from the condensation of salicylaldehyde and *N*-(2-aminoethyl)aziridine or *N*-(3-aminopropyl)aziridine interact with nickel(II) and copper(II).

Experimental Section

Magnetic Measurements.—Magnetic susceptibilities were measured either by the Gouy method or by the nmr method of Evans[17] as modified by Fritz and Schwarzhans.[18] Nmr measurements were made in 90:10 benzene–cyclohexane solutions using tris(2,4-pentanedionato)iron(III) as calibrant assuming μ_{eff} = 5.95 BM.[19] Ligand corrections were made using Pascal's constants.

Infrared Spectra.—Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using Nujol mulls or potassium bromide pellets.

Electronic Spectra.—Electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. Spectra of solids were recorded using Nujol mulls on filter paper.

Molecular Weights.—Molecular weight data were obtained with a Mechrolab Model 301A vapor pressure osmometer, calibrated with solutions of benzil.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by M-H-W Laboratories, Garden City, Mich.

We gratefully acknowledge the contribution by Dow Chemical Co., Midland, Mich., of *N*-(2-aminoethyl)aziridine and *N*-(2-cyanoethyl)aziridine.

N-(2-Aminoethyl)aziridine was either used without further purification or distilled from a mixture of itself and the trimer and tetramer of aziridine. Distillations were done at 100 mm and the fraction boiling at 69–73° was taken. Purity was checked by gas chromatography. Particular care was taken to show the absence of ethylenediamine by comparing chromatograms of the ligand with those of a mixture of ethylenediamine and the ligand.

N-(3-Aminopropyl)aziridine was synthesized from *N*-(2-cyanoethyl)aziridine by the method of Salerni and Clark.[20] Our yields were 10–15%.

Syntheses. **Bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}nickel(II), [Ni(salAEA)$_2$].**—To a suspension of 4.06 g (0.0121 mol) of bis(salicylaldehydo)diaquonickel(II) in 50 ml of 1-butanol was added 10 ml of 1-butanol containing 2.08 g (0.0242 mol) of *N*-(2-aminoethyl)aziridine. After refluxing for about 8 hr, the volume was reduced to about 30 ml with a rotary evaporator and petroleum ether (bp 30–60°) was added. A yield of 4.32 g (81.6%) of green product was isolated by filtration and dried *in vacuo*. This reaction was also run in ethanol and methanol.

Bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}copper(II), [Cu(salAEA)$_2$].—To 1.53 g (0.00500 mol) of bis(salicylaldehydo)copper(II) partially dissolved in 125 ml of benzene, 1.00 g (0.0116 mol) of *N*-(2-aminoethyl)aziridine dissolved in 10 ml of benzene was added. During addition, the solution changed from olive green to dark green. This solution was then refluxed for about 2 hr during which time 80–100 ml of benzene–water azeotrope and solvent was removed in a distillation receiver. The reaction mixture was taken nearly to dryness with a rotary evaporator yielding the crude product. Recrystallization from 1:1 benzene–petroleum ether gave 2.13 g (96%) of the pure green solid.

Bis{*N*-[3-(1-aziridinyl)propyl]salicylaldimino}nickel(II), [Ni(salAPA)$_2$.]—To a suspension of 0.842 g of bis(salicylaldehydo)diaquonickel(II) (0.00250 mol) in 20 ml of 1-butanol was added 10 ml of 1-butanol containing 0.500 g (0.00500 mole) of *N*-(3-aminopropyl)aziridine. After refluxing for 1.5 hr the reaction mixture was cooled and filtered giving 0.939 g (81.0%) of the yellow product.

This compound was also prepared by the reaction of salicylaldehyde and *N*-(3-aminopropyl)aziridine with nickel(II) acetate tetrahydrate in a 2:2:1 mole ratio. Methanol, ethanol, or 1-butanol can be used as solvent in either procedure.

Bis{*N*-[3-(1-aziridinyl)propyl]salicylaldimino}copper(II), [Cu(salAPA)$_2$].—To 1.53 g (0.00500 mol) of bis(salicylaldehydo)copper(II) dissolved in 125 ml of benzene was added 1.16 g (0.0116 mol) of *N*-(3-aminopropyl)aziridine dissolved in 10 ml of benzene. This mixture was refluxed about 3 hr during which time approximately 90 ml of benzene–water azeotrope and solvent was removed in a distillation receiver. The reaction mixture was evaporated to a green oil with a rotary evaporator and then redissolved in a minimal amount of benzene. Addition of petroleum ether and refrigeration for 1 day caused crystallization of the green product. Additional fractions could be obtained by adding petroleum ether to the filtrate until a nearly quantitative yield was obtained. The product was dried *in vacuo* at room temperature. The product melted at 45–50°.

Bis(salicylidene)ethylenediiminenickel(II), [Ni((sal)$_2$en)].—To a suspension of 3.01 g of nickel(II) acetate tetrahydrate (0.121 mol) in 20 ml of 1-butanol was added 10 ml of 1-butanol containing 2.96 g of salicylaldehyde (0.0242 mol) and 10 ml of 1-butanol containing 2.08 g (0.0242 mol) of *N*-(2-aminoethyl)aziridine. The reaction mixture was refluxed for about 10 hr and then cooled. Upon cooling, the red product crystallized and was isolated by filtration. Yields for this reaction have been as high as 40%. Decreasing the amount of diamine in the reaction mixture decreased the yield. For example, if the nickel(II) ion:salicylaldehyde:diamine ratio was 1:2:1, the yield was 10%.

Bis(salicylidene)ethylenediiminecopper(II), [Cu((sal)$_2$en)].—To 150 ml of absolute methanol solution of 6.00 g (0.0300 mol) of copper(II) acetate monohydrate, 7.22 g (0.0591 mol) of salicylaldehyde and 5.70 g (0.0661 mol) of *N*-(2-aminoethyl)aziridine, each dissolved in a small amount of absolute methanol, were added. After reflux for 24 hr, the solution was cooled in a refrigerator for 2 days after which 0.97 g of [Cu((sal)$_2$en)] was isolated by filtration (10%).

Reaction of Nickel(II) Carbonate, Salicylaldehyde, and *N*-(2-Aminoethyl)aziridine.—A mixture of 1.44 g (0.0121 mol) of nickel(II) carbonate, 2.96 g (0.0242 mol) of salicylaldehyde, and 2.08 g (0.0242 mol) of *N*-(2-aminoethyl)aziridine was refluxed in 40 ml of 1-butanol for 12 hr. After cooling, a small amount of undissolved nickel(II) carbonate was removed by filtration. Upon cooling the solution, red [Ni((sal)$_2$en)], 0.69 g, crystallized. From the filtrate, after adding small amounts of ether and water, 1.34 g of green [Ni(salAEA)$_2$] was isolated. The identity of the products was determined by comparison of their infrared spectra with those of authentic samples.

Conversion of [Ni(salAEA)$_2$] to [Ni((sal)$_2$en)].—(a) A solution of 1.0 g of [Ni(salAEA)$_2$] in 20 ml of 1-butanol containing 1 ml of concentrated acetic acid was refluxed for 3 hr. A yield of 0.080 g of [Ni((sal)$_2$en)], identified by its ir spectrum, was isolated by filtration. The yield was about 11%.

(b) A 2.00-g sample of [Ni(salAEA)$_2$] (0.00456 mol) was refluxed 24 hr with 0.19 g of *p*-toluenesulfonic acid (0.00100 mol) in 20 ml of 1-butanol. Concentration of the solution yielded 0.470 g of red [Ni((sal)$_2$en)] by filtration, 31.8% yield.

Results and Discussion

Two types of reaction have been observed for the formation of transition metal complexes of the Schiff bases derived from salicylaldehyde and *N*-(aminoalkyl)aziridines. The first leads to the formation of a neutral complex of the expected Schiff base condensation product as shown in eq 1. The second type involves the reaction of the metal acetate with salicylaldehyde and *N*-(2-aminoethyl)aziridine and leads to the formation of complexes of bis(salicylidene)ethylenediimine, (sal)$_2$en, eq 2.

The reaction of salicylaldehyde with *N*-(2-aminoethyl)aziridine in benzene gives the expected Schiff base, 1. The Schiff base melts near room temperature and has been identified by its nmr spectrum. An nmr spectrum of 1 in deuteriochloroform shows a complex pattern centered at −1.4 ppm from TMS of relative intensity 4, assigned to the aziridine ring protons, a

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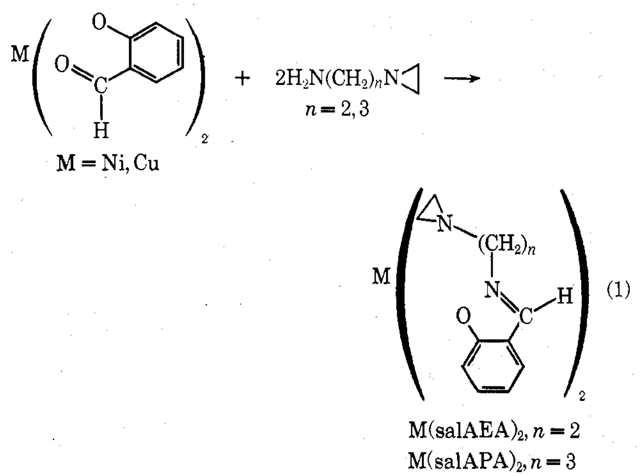
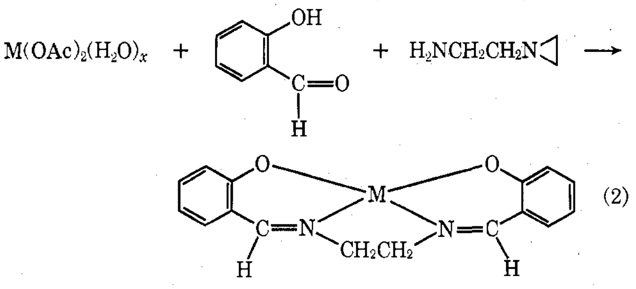
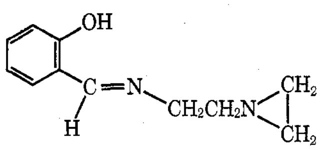




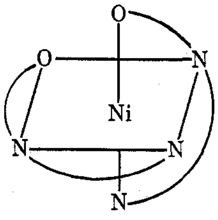


1

complex pattern centered at −3.2 ppm from TMS of relative intensity 4 assigned to the $=NCH_2CH_2N<$ protons, a complex pattern at −7.1 ppm from TMS of relative intensity 4 assigned to the aromatic protons, a single peak at −8.4 ppm from TMS of relative intensity 1 assigned to the –CH=N– proton of the aldimine function, and a broad resonance at −13 ppm from TMS of relative intensity slightly less than 1 assigned to the phenolic proton.

Reaction of the synthesized ligand with metal salts is not generally successful; however, small yields of both $[Ni(salAEA)_2]$ and $[Ni((sal)_2en)]$ can be obtained from the reaction of benzene solutions of **1** with alcohol solutions of nickel(II) acetate tetrahydrate. The complex of the tridentate ligands is isolated after short reaction time at low temperature. Long reaction time and higher temperature favor formation of $[Ni((sal)_2en)]$.

Nickel Complexes.—The reaction of AEA with bis(salicylaldehydo)diaquonickel(II) in methanol, ethanol, or 1-butanol at reflux temperature leads to the formation of bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}nickel(II), $[Ni(salAEA)_2]$. The yields are about 80% in each solvent. The nickel(II) complex prepared from *N,N*-dimethylethylenediamine and salicylaldehyde is believed to have the peripheral structure, **2**.[5,6]



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Selective formation of this isomer is reasonable considering the planarity of the conjugated portion of the ligand and the size of the N–N chelate ring. The electronic spectrum of $[Ni(salAEA)_2]$ in $CHCl_3$ and in Nujol mulls supports the assignment of a six-coordinate structure both in the solid state and in solution. The absence of spin-allowed transitions below 8000 cm^{-1} rules out the possibility of five-coordinate structure.[7,8,12] Indeed, the spectra compare well qualitatively with those reported by Sacconi for similar complexes.[6] The band at 11,300 cm^{-1} is 770 cm^{-1} higher in energy than the corresponding band for the *N,N*-dimethyl complex[6] so the lesser steric bulk of the aziridine ring compared with the acyclic analog may cause some increased field strength. The magnetic moment of 3.07 BM also supports assignment of a six-coordinate structure. The characterization of this compound is complicated by one fact, the appearance of an ir absorption peak at 3620 cm^{-1}. This peak remains unassigned and is seemingly inconsistent with the other data. Peaks at 1630, 1590, and 1525 cm^{-1} are indicative of the salicylaldimine function. The molecular weight is confirmed in solution (Table I) and by the observation of parent ion peaks in the mass spectrum at 436 and 438.

The reaction of APA with bis(salicylaldehydo)diaquonickel(II) in methanol, ethanol, or 1-butanol at reflux temperatures yields bis{*N*-[3-(1-aziridinyl)propyl]salicylaldimino}nickel(II), $[Ni(salAPA)_2]$, in about 80% yield. This bright yellow complex is monomeric and six-coordinate on the basis of its molecular weight, magnetic moment, and electronic spectrum. An X-ray structure determination of bis(*N*-γ-dimethyl-

TABLE I

ANALYTICAL AND MOLECULAR WEIGHT DATA FOR THE COMPLEXES

		% carbon		% hydrogen		% nitrogen		Mol wt	
Compd	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Ni(salAEA)_2]$	Green	60.44	60.36	5.99	6.29	12.82	12.54	437	465[a]
$[Ni(salAPA)_2]$	Yellow	61.96	61.90	6.50	6.46	12.04	12.14	465	467[b]
$[Ni((sal)_2en)]$[c]	Red	59.13	59.20	4.34	4.37	8.62	8.55		
$[Cu(salAEA)_2]$	Green	59.78	60.48	5.93	6.02	12.68	12.48	442	461[d]
$[Cu((sal)_2en)]$[e]	Green	58.26	58.48	4.28	4.28	8.49	8.51		
$[Cu(salAPA)_2]$	Green	61.32	61.37	6.43	6.57	11.92	11.69	470	436[f] 500[g]

[a] By vapor pressure osmometry, 0.0202 *M* in $CHCl_3$. [b] By vapor pressure osmometry, 0.0205 *M* in $CHCl_3$. [c] Prepared by reaction of nickel(II) acetate, salicylaldehyde, and *N*-(2-aminoethyl)aziridine. [d] By vapor pressure osmometry, 0.0104 *M* in C_6H_6. [e] Prepared by reaction of copper(II) acetate, salicylaldehyde, and *N*-(2-aminoethyl)aziridine. [f] By vapor pressure osmometry, 0.00743 *M* in $ClCH_2CH_2Cl$. [g] By vapor pressure osmometry, 0.0048 *M* in C_6H_6.

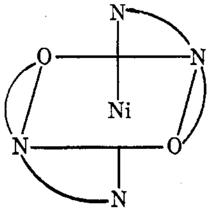
TABLE II

MAGNETIC MOMENTS

Compd	Temp, °C	μ_{eff},[a] BM
[Ni(salAEA)$_2$]	17	3.07 ± 0.02
[Ni(salAPA)$_2$]	24	3.20 ± 0.05
[Cu(salAEA)$_2$]	25	1.86
	40	1.89[b]
[Cu(salAPA)$_2$]	40	1.96[c]

[a] Measured by Gouy method on solid sample unless designated otherwise. [b] Measured by nmr in 9:1 benzene–cyclohexane. [c] Measured by nmr in 9:1 1,2-dichloroethane–cyclohexane.

aminopropylsalicylaldimino)nickel(II) shows that when the N–N chelate ring contains six atoms, a facial isomer, **3**, is produced.[4,21] This is the one isomer, of six facial possibilities which is centrosymmetric and presumably least sterically hindered. The assignment of the facial isomeric form, **3**, to [Ni(salAPA)$_2$] is supported by the fact that the molar absorptivities of the ligand field transitions are lower than those of [Ni(salAEA)$_2$]. Attempts to obtain structural information from the nmr spectra of these complexes have not been successful due to the breadth of the peaks and limited solubility.



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The reaction of nickel(II) acetate tetrahydrate with salicylaldehyde and *N*-(2-aminoethyl)aziridine in a 1:2:2 mole ratio gives 30–40% yields of bis(salicylidene)ethylenediiminenickel(II), [Ni((sal)$_2$en)]. This product has been characterized by elemental analysis, electronic and vibrational spectroscopy, nuclear magnetic resonance spectroscopy, and comparison with an authentic sample prepared from ethylenediamine.[22] Mass spectroscopy also confirms the identity of this product.

The formation of [Ni((sal)$_2$en)] is the result of a new type of deamination reaction of the aziridine ring. It has previously been found that facile deamination of N-substituted aziridines can be effected by treatment with *m*-chloroperbenzoic acid giving olefin and nitroso compounds.[23,24] We have been unable to determine the identity of the other products of this reaction. Since this reaction is similar to that which produces [Ni(salAEA)$_2$], except that it contains the acetate ion, it is quite likely that acetate ion is involved in opening of the aziridine ring. Opening of the aziridine ring by nucleophilic reagents is known to be facilitated by the presence of electron-withdrawing groups on the aziridine nitrogen.[25,26] The metal ion presumably plays the role of ring activator facilitating nucleophilic attack.

Our results support the functioning of [Ni(salAEA)$_2$] as the reactive intermediate. When the amount of AEA is decreased below the ratio of 1:2:2, nickel acetate:salicylaldehyde:AEA, the yield of [Ni((sal)$_2$en)] decreases. A ratio of 1:2:1 gives a 10% yield of [Ni((sal)$_2$en)]. When [Ni(salAEA)$_2$] is treated with acetic acid or *p*-toluenesulfonic acid, a 30% yield of [Ni((sal)$_2$en)] is obtained. It is very significant that a similar reaction will *not* take place using APA in place of AEA. Reaction of nickel(II) acetate tetrahydrate, salicylaldehyde, and APA gives a 70% yield of yellow [Ni(salAPA)$_2$]. Reaction of [Ni(salAPA)$_2$] with acetic acid gives no bis(salicylidene)-1,3-propanediiminenickel(II), the expected product of a deamination reaction.

Copper Complexes.—The reaction of bis(salicylaldehydo)copper(II) with AEA in benzene results in formation of bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}copper(II), [Cu(salAEA)$_2$]. The same procedure gives bis{[*N*-[3-(1-aziridinyl)propyl]salicylaldimino}copper(II), [Cu(salAPA)$_2$], when APA is used as the diamine. The spectra of these complexes (see Table III) in the solid state correspond closely to those observed for copper(II) complexes known to have square-planar structures.[11,27–29] Tetrahedral four-coordination is not likely since ligand field bands are not observed below 12,000 cm^{-1}.

TABLE III

ELECTRONIC SPECTRA

Compd	Solvent	$\bar{\nu}_{\max}$, cm^{-1} ($\epsilon_{\max}$)
[Ni((sal)$_2$en)]	Solid	~19,000, ~22,500, 23,900, 30,400, 41,200
[Ni(salAPA)$_2$]	Solid	~8510 br, sh, 11,400, 18,900 sh, 26,700, 41,700
	CHCl$_3$	~8510 br, sh, 11,200 (6.34), 12,600 sh, 18,200 (12.3) sh, 26,700 (8950)
[Ni(salAEA)$_2$]	Solid	~8510 sh, 11,200 br, 12,500 sh, 17,500, 26,000, 41,700
	CHCl$_3$	~8700 br, sh, 11,300 (35.2), 17,800 (18.0), 26,700 (10,000)
[Cu(salAEA)$_2$]	Solid	~15,000 sh, 16,400, 27,300, 33,200
	C$_6$H$_6$	16,200 (103)
	ClCH$_2$CH$_2$Cl	14,800 (116), 27,000 (9440), 25,500 sh (7880)
[Cu(salAPA)$_2$]	Solid	15,800 br, 27,300, 33,300, 37,000 sh, 40,800
	C$_6$H$_6$	~13,600 sh, 15,500 (74.5)
	ClCH$_2$CH$_2$Cl	~13,800 sh, 15,400 (86.9), 27,500 (9310), 33,300 (7490), 37,600 sh, 41,500 sh

In benzene and 1,2-dichloroethane solutions, [Cu(salAPA)$_2$] shows a distinct shoulder on the low-energy side of the more intense d–d transition. This may be indicative of a coordination number of 5 or 6 for this species in these solvents.[28] Molecular weight measurements of [Cu(salAPA)$_2$] in benzene and 1,2-dichloroethane at concentrations comparable to those at which the spectra were run indicate that dimerization is minimal, if indeed existent, at these concentrations. The solvent dependence of the ligand field transition energy, particularly for [Cu(salAEA)$_2$], is reminiscent

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of the behavior of bis(*N*-methylsalicylaldimino)copper(II).[30]

The reaction of copper(II) acetate monohydrate with salicylaldehyde and *N*-(2-aminoethyl)aziridine in methanol has resulted in low yields (always 10% or less) of bis(salicylidene)ethylenediiminecopper(II), [Cu((sal)$_2$en)]. The low yield in this reaction supports the contention that the six-coordinate complex may be the intermediate as in the corresponding reaction with nickel(II). The concentration of six-coordinate copper(II) species is not likely to be large and perhaps the course of the reaction is different from that of the nickel(II) complex. As is true with nickel, the occurrence of a ring-opening reaction with [Cu(salAPA)$_2$] has not been detected.

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Cationic Nickel Nitrosyl Complexes with Two "Tripod-Like" Aliphatic Triphosphines[1]

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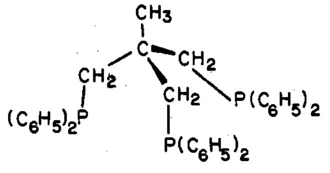
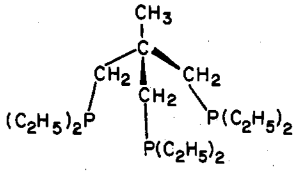
The deep red, diamagnetic, uni-univalent electrolytes [Ni(tpp)NO]X and [Ni(tep)NO]X (where X = Cl, Br, I, BF$_4$, B(C$_6$H$_5$)$_4$; tpp and tep = the "tripod-like" triphosphines $CH_3C(CH_2PPh_2)_3$ and $CH_3C(CH_2PEt_2)_3$, respectively) result from the reactions of nickel(II) halides, nitrite ion, and the triphosphine ligands in absolute ethanol. An X-ray structural determination of [Ni(tep)NO]BF$_4$ has shown that the nickel atom is surrounded in a pseudotetrahedral fashion by three phosphorus atoms and a linearly bonded nitrosyl group.

Introduction

During our investigations into the structures of five-coordinate nickel(II) complexes resulting from polyphosphines, we observed[2] that the "tripod-like" triphosphines tpp and tep react with nickel(II) halides in ethanol to form planar Ni(ligand)X$_2$ complexes in which the triphosphine functions only as a bidentate ligand. However, the same reagents in the presence of nitrite ion give intensely colored solutions from which deep red complexes of elemental composition [Ni(ligand)(NO)]X (X = Cl, Br, I) crystallize. The presence of the nitrosyl group is indicated by a strong infrared absorption at *ca.* 1760 cm^{-1}, which may be assigned to the N–O stretching frequency. This reaction appears to be analogous to Feltham's studies[3,4] in which the tetrahedral Ni(PPh$_3$)$_2$X$_2$ complexes were mixed with nitrite ion and the nitrosyl complexes Ni(PPh$_3$)$_2$(NO)X were isolated. This paper reports the preparation and characterization of two series of Ni(triphosphine)(NO)X complexes (X = Cl, Br, I, BF$_4$, B(C$_6$H$_5$)$_4$) and discusses the data in terms of the ambiguities involved in assigning formal oxidation states to nickel and the nitrosyl group.



tpp



tep

Experimental Section

Reagents.—The nickel(II) salts, sodium tetraphenylborate, and absolute ethanol were reagent grade and were used without further purification. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, tpp, was prepared according to the procedure of Hewertson and Watson[5] by Strem Chemicals, Inc., and by Orgmet, Inc., on a custom order basis. *Anal.* Calcd for $C_{41}H_{39}P_3$:[6] C, 78.85; H, 6.25; P, 14.90. Found: C, 78.90; H, 6.21; P, 15.04. The corresponding diethylphosphino ligand, tep, was prepared by a procedure analogous to that for tpp by Orgmet, Inc. The $CH_3C(CH_2PEt_2)_3$ ligand is a clear liquid that is extremely sensitive to oxidation; thus, all of the handling and syntheses involving the tep ligand were conducted in a dry, oxygen-free atmosphere (usually purified nitrogen or argon).

Isolation of the Complexes.—All of the steps in the preparations of the complexes were executed in an oxygen-free atmosphere. For the tep complexes, the dissolved oxygen was removed from the solvents before the ligand was added. The solid complexes were collected in a closed filter funnel on a sintered-glass frit and were dried with a stream of nitrogen.

[Ni(tep)(NO)]I.—Anhydrous nickel(II) iodide was prepared, *in situ*, by adding 2,2-dimethoxypropane (5 ml) to the absolute ethanol solution that resulted from mixing sodium iodide (0.49 g, 3.28 mmol) and Ni(NO$_3$)$_2$·6H$_2$O (0.48 g, 1.64 mmol) and filtering off the sodium nitrate. The tep ligand was added and the resulting solution was refluxed for 15 min. Then potassium nitrite (0.56 g, 6.56 mmol), which was partially dissolved in 20 ml of ethanol, was added to the solution. The mixture was stirred for 12 hr at room temperature; then the ethanol was evaporated and the compound was extracted from the solid with dichloromethane. A red-orange solid, which was recovered by evaporating the CH$_2$Cl$_2$, was recrystallized from CH$_2$Cl$_2$–*n*-C$_5$H$_{12}$ (5 ml of each).

[Ni(tep)(NO)][B(C$_6$H$_5$)$_4$].—An ethanol solution of NaB(C$_6$H$_5$)$_4$ was added slowly to an ethanol solution of [Ni(tep)(NO)]I.

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