Monoquaternized Pyrazinium Cations as Examples of 'Non-basic' Nitrogen-Donor Ligands

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The reaction of some representative metal halides with the halides of N-methylpyrazinium, N(1)-methyl-2,5-dimethylpyrazinium, and N(1)-methyl-2,6-dimethylpyrazinium was investigated to establish the coordinating ability of these monoquaternized diaza-heterocyclic cations (L^+). It was found that N-methylpyrazinium readily coordinates to metal ions forming zwitterionic complexes of the types $[MX_3(L^+)]$ (where M is Co(II), Cu(II), Zn(II) and X is Cl, Br) or $[MX_4(L^+)_2]$ (where M is Ni(II) and X is Cl, Br). The mono-hindered N(1)-methyl-2,5-dimethylpyrazinium, however, combines with the same metal ions to give only $[MX_3(L^+)]$ complexes, while the doubly-hindered N(1)-methyl-2,6-dimethylpyrazinium behaves as a counterion in salts of the type $(L^+)_2[MX_4]$. The facile complexation of the N-methylpyrazinium cation-ligand sharply contrasts with the very low basicity of the parent pyrazine molecule ($pK_a = 0.65$) and with the complete lack of proton acceptor properties of its monoquaternized derivatives.

Introduction

The coordinating ability of cationic N-donor ligands toward metal ions has been extensively investigated by Quagliano, Vallarino, and coworkers. These studies, which focused chiefly on the divalent metal ions of the First Transition Series (d^5 to d^{10} configurations), have included primary [1], secondary [2], and tertiary cationic amines [3–8] among which the compact, cage-like derivatives of 1,4-diaza[2.2.2]bicyclooctane have proved to be exceptionally varied and interesting. Marcotrigiano, Menabue, and Pellacani [9–12] have also reported numerous metal complexes of cationic secondary amines, which exhibit an unusual variety of stereochemical arrangements. This body of work clearly shows that the presence of a positive charge on a ligand does not prevent its coordination to a metal ion, even when the donor N-atom is immediately adjacent to the charged site [13]. In the presence of anions with good coordinating ability (X = halide or nitrate), positively charged ligands (L^+) usually tend to form zwitterionic complexes with either a 1:1 or a 2:1 ligand-to-metal ratio. Highly charged cationic complexes with 4:1 and 6:1 ligand-to-metal ratios may be obtained when the donor groups are primary amines, in the absence of strongly coordinating anions.

The cationic ligands considered in these previous investigations had two features in common: They were all aliphatic in character and all, except 1,1,1-trimethylhydrazinium [13], contained a N-donor atom separated from the positive site by an intervening chain of two or more saturated carbon atoms. The question therefore remained, whether a similar coordinating ability might be exhibited by N-heterocyclic systems in which the positive charge is somewhat delocalized to include the potential donor atom. To address this question, we set out to investigate the complexing ability of several monoquaternized diaza-heterocyclic compounds. For the present work the system of choice was pyrazine, the monoquaternized derivatives of which again contain a potential N-donor atom two carbon atoms removed from the positively charged site, but with the added feature of strong possible interactions arising from the aromatic character of the ring.

Pyrazine, the 1,4-diaza-analog of pyridine, is a highly symmetrical molecule whose interatomic distances and π-electron densities at the carbon atoms are very similar to those of pyridine [14]. Despite these structural similarities, however, pyrazine and pyridine differ markedly in their nucleophilic character. Pyridine itself is a moderately strong base toward proton acids ($pK_a = 5.2$) and its mono- and di-methyl-substituted derivatives, the picolines and lutidines, are even stronger. Pyrazine, in contrast, is an extremely weak base which exhibits only monoprotic character. Its potentiometric titration gives a single end point at one-mole-equivalent of H^+ ions ($pK_{a1} = 0.65$) and only salts of the monoprotonated

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pyrazinium cation may be isolated even from strongly acidic solutions [15]; the second protonation constant of pyrazine has been estimated to have a rather large negative value ($pK_{a2} = -5.6$) [16]. Methyl substitution at the ring-carbon atoms slightly increases the basicity of the pyrazine system but the substituted compounds still behave as extremely weak monoprotic bases (the pK_{a1} is 1.40 for the mono- and 1.90 for the dimethyl-derivatives). In general, once one of the two ring-nitrogen atoms has become positively charged through quaternization, protonation of the other ring-nitrogen becomes virtually impossible. Diquaternization of the pyrazine system can be achieved with strong alkylating agents, such as triethyloxonium tetrafluoroborate. The resulting di-cations, however, are extremely reactive and readily form radical mono-cations upon electrochemical reduction [17].

The monovalent character of pyrazine toward proton acids and the relative instability of its alkyl di-cations sharply contrast with its behavior toward metal ions, first established some twenty years ago by Nyholm, Lewis, and Lever [18, 19]. These investigators prepared a number of very stable polymeric complexes of copper(I), cobalt(II), and nickel(II), in which pyrazine acts as a bridging ligand symmetrically linked to two equivalent metal ions. The electronic spectra of these complexes indicate that pyrazine, regardless of its very low basicity, must occupy in the spectrochemical series of these transition metal ions a position very close to that of pyridine. Also, some pyrazine complexes of Ni(II) halides exhibit an unusual 'anti-spectrochemical series' behavior, in the sense that their average Dq value increases as the strength of the halide ligands decreases, suggesting an evercompensating effect on the part of the coordinated pyrazine. Metal-to-ligand π-back-bonding has been postulated to account for the stability and anomalous electronic spectral features of these complexes [19]. The interpretation of the electronic spectra of pyrazine-bridged complexes is, however, somewhat complicated by the possibility of extended electron delocalization which arises in chain-like polymeric complexes of aromatic ligands. For some pyrazine-bridged Cu(II) species, such electron delocalization is sufficiently strong to result in either ferromagnetic or antiferromagnetic behavior [20–24].

A study of the coordinating properties of monoquaternized pyrazinium cations thus appeared to be of interest for several reasons. First, these cations offer the possibility of strong interaction between the two nitrogen atoms in 1,4-positions, and thus are especially relevant to our investigation of the effect of positive charge on the coordinating ability of heteroaromatic ligands. Second, a study of these systems would permit a direct comparison of the ligating properties of pyrazinium and its sterically hindered derivatives with those of the similarly hindered pyridines previously investigated by us [25]. Finally, if metal complexes of monoquaternized pyrazinium could be obtained, the intrinsic donor character of its N-donor atom might be evaluated in the absence of complicating factors due to a polynuclear bridged structure.

Experimental

Starting Materials

Pyrazine, 2,5-dimethylpyrazine, and 2,6-dimethylpyrazine were reagent grade commercial products (Aldrich). Metal salts were anhydrous, except for $CuCl_2 \cdot 2H_2O$ and $NiI_2 \cdot 6H_2O$; the latter compound was repeatedly washed before use with small volumes of ice-cold ethanol, to remove the iodine and other impurities formed by air-oxidation and hydrolysis. The bright-green crystals of $NiI_2 \cdot 6H_2O$ were then dissolved in warm ethanol containing 5% of triethylorthoformate and the solution was used immediately to minimize decomposition.

Preparations and Properties of the Ligands

N-Methylpyrazinium iodide was prepared by a previously described method [26]; it was obtained as bright yellow needles, m.p. 140 °C (literature, 136 °C). *Anal*: calc. for $C_5H_7N_2I$: N, 12.63; I, 57.16. Found: N, 12.68; I, 56.90%. *N-Methylpyrazinium chloride and bromide* were prepared by ion exchange in aqueous solution (3 g in 50 ml) using Dowex-1-X8 anion exchange resin, 100–200 mesh. The absence of I^- in the effluants was monitored by spot-testing with lithium tetrachloropalladate and Fe(III) sulfate/starch indicator. The effluants were taken to dryness under reduced pressure in a rotary evaporator and the residues were recrystallized from ethanol-ether. The very hygroscopic off-white powders thus obtained were filtered off in a dry atmosphere, washed with diethylether, and dried *in vacuo*. *N-methylpyrazinium chloride*: m.p. 131 °C (decomp.). *Anal.* Calcd. for $C_5H_7N_2Cl$: N, 21,45; Cl, 27.17. Found: N, 21.56; Cl, 27.04%. *N-methylpyrazinium bromide*: m.p. 171 °C. *Anal.* Calc. for $C_5H_7N_2Br$: N, 16.01, Br, 45.67. Found: N, 15.95; Br, 45.44%.

N-methyl-2,5-dimethylpyrazinium iodide, chloride, and bromide were prepared similarly to the pyrazine analogs. The iodide was obtained as fine pale yellow needles, m.p. 222 °C. *Anal.* Calcd. for $C_7H_{11}N_2I$: I, 50.74. Found: I, 49.84%. The chloride and bromide formed colorless needles when crystallized from rigorously anhydrous solvents in a dry atmosphere; however, these rapidly changed to a glassy mass when exposed to atmospheric moisture.

N(1)-methyl-2,6-dimethylpyrazinium iodide was prepared similarly to the pyrazine analog; it was obtained as long bright-yellow needles, m.p. 218 °C. *Anal.* Calcd. for $C_7H_{11}N_2I$: I = 50.74. Found: I = 50.1%.

All compounds were very soluble in water and alcohols, soluble in acetone, insoluble in diethylether, benzene and hexane. Their infrared and visible-ultraviolet absorption spectra, as well as their ^1H NMR spectra, agreed with those reported in the literature [27].

Preparation and Characterization of the Complexes

The complexes were prepared by the following general procedure. A solution of the ligand halide in ethanol containing 5% triethylorthoformate was heated to 70 °C and added slowly and with stirring to a filtered hot solution of the metal salt in ethanol-triethylorthoformate. The ligand-to-metal ratio was usually kept in the range 0.8–1.5. Higher ligand-to-metal ratios, or inverting the order of mixing (*e.g.* adding the metal to the ligand) generally yielded the same products but in less pure form. Most complexes precipitated as well-formed crystals either immediately or upon cooling; if precipitation did not occur spontaneously, it was induced by the addition of diethylether and scratching. The crystals were filtered, washed with diethylether, and dried *in vacuo.* Beautifully crystalline mixed-metal complexes were easily obtained from solutions containing Co(II)–Zn(II) chlorides.

The complexes were characterized by elemental analyses, magnetic moments, infrared spectra, and electronic absorption spectra. The relevant data are collected in Tables I–III.

Physical Measurements

Infrared spectra (4000–190 cm^{-1}) were recorded with Perkin-Elmer Models 580 and 283 spectrophotometers, using a combination of hexachlorobutadiene and Nujol mulls. Electronic absorption spectra (1800–320 nm) were recorded with a Cary Model 17 spectrophotometer; solid samples were examined by diffuse reflectance as well as by transmission using Nujol mulls with MgO as the reference. Magnetic susceptibility measurements were carried out at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the calibration standard. ^1H NMR spectra of the ligands were taken with a Varian CFT-20 Fourier-Transform NMR spectrometer at 80 MHz in D_2O solution. Thermogravimetric measurements were obtained with a Perkin-Elmer TGS Thermogravimetric System equipped with dry helium flow. Metals were analyzed by EDTA titration; halogens were determined by the Volhard method; microanalyses (C, H, and N) of selected samples were performed by Atlantic Microlab, Atlanta, Georgia.

Results and Discussion

The halides of N-methylpyrazinium and related heterocyclic cations combine with the corresponding halides of Co(II), Ni(II), Cu(II), and Zn(II) to yield a variety of crystalline products whose stoichiometry and structure depend on the heterocyclic cation, the metal-halide combination, and the reaction conditions. These products fall into two general groups, corresponding to either a 1:1 or a 2:1 ligand-to-metal ratio; no species containing more than two quaternized pyrazinium cations per metal ion have been observed.

Compounds Containing One N-methylpyrazinium Cation per Metal Ion

Well-crystallized compounds having the general formula $MX_2 \cdot (L^+X^-)$ are obtained from the chlorides of Co(II), Cu(II), and Zn(II) with N-methylpyrazinium chloride, and from the bromides of Co(II) and Zn(II) with N-methylpyrazinium bromide. The colors, melting points, and analytical data of these compounds are listed in Table I; their structural elucidation is based on the following evidence.

The electronic (d–d) absorption spectra of the Co(II) species (Table III) are clearly diagnostic of a tetrahedral geometry. Furthermore, the pattern

TABLE I. Selected Properties and Analytical Data of Zwitterionic Complexes Containing N-Methylpyrazinium Ligands.

Compound[a]	Color	m.p.[b] (°C)	ν(M–X)[c] (cm^{-1})	Analyses: Metal% Calcd.	Analyses: Metal% Found	Analyses: Halogen% Calcd.	Analyses: Halogen% Found
$[CoCl_3(pyrCH_3^+)]$	green	208	340s,282s	22.63	22.4	40.84	39.9
$[CoCl_3(2,5\text{-}diMepyrCH_3^+)]$	green	155	323s,288sh	20.43	20.9	36.87	36.8
$[ZnCl_3(pyrCH_3^+)]$	bone	184	320–310s,285m	24.49	24.0	39.86	39.1
$[ZnCl_3(2,5\text{-}diMepyrCH_3^+)]$	bone	136	310s,285m	22.16	22.0	36.07	35.8
$[CuCl_3(pyrCH_3^+)]$	olive green	155	290s	23.78	24.1	40.13	39.9
$[CoBr_3(pyrCH_3^+)]$	green	209	270s,250s,220sh	14.96	14.7	60.88	59.9
$[CoBr_3(2,5\text{-}diMepyrCH_3^+)]$	green	188	255s,210w	13.97	13.5	56.83	56.5
$[NiCl_4(pyrCH_3^+)_2]$	yellow	250	240s	15.02	16.1	36.29	38.1
$[NiBr_4(pyrCH_3^+)_2]$	rust	250	210s	10.33	10.4	56.21	56.0

[a] $pyrCH_3^+$ = N-Methylpyrazinium; $2,5\text{-}diMepyrCH_3^+$ = N-Methyl-2,5-dimethylpyrazinium; $2,6\text{-}diMepyrCH_3^+$ = N-Methyl-2,6-dimethylpyrazinium. [b] Compounds generally decompose upon melting. [c] s = strong; m = medium; w = weak; sh = shoulder.

TABLE II. Selected Properties and Analytical Data for Halometallates of the N-methylpyrazinium Cations and Substituted Analogs.

Compound[a]	Color	m.p.[b] (°C)	$\nu(M-X)$[c] (cm^{-1})	Magnetic moment μ_{eff} (B.M.)	Analyses			
					Metal%		Halogen%	
					Calcd.	Found	Calcd.	Found
$(\mathrm{pyrCH_3^+})_2[\mathrm{CoCl_4}]$	pale blue	137	290s	4.54	15.06	15.0	36.29	36.1
$(\mathrm{pyrCH_3^+})_2[\mathrm{CoBr_4}]$	grayish blue	132	220s	4.62	10.36	10.2	56.19	56.0
$(\mathrm{pyrCH_3^+})_2[\mathrm{CoI_4}]$	olive green	127	190s	4.80	7.79	8.2	67.07	67.0
$(\mathrm{pyrCH_3^+})_2[\mathrm{CuBr_4}]$	violet-brown	162		1.98	11.08	10.9	52.2	52.0
$(\mathrm{pyrCH_3^+})_2[\mathrm{ZnI_4}]$	palc yellow	128		Diamagn.	8.56	9.1	66.51	65.9
$(\mathrm{2,5\text{-}diMepyrCH_3^+})_2[\mathrm{CoI_4}]$	olive green	101	190s		7.24	7.1	62.44	62.2
$(\mathrm{pyrCH_3^+})_n\{\mathrm{NiCl_3}\}_n$	pale yellow	250	255s,215m		22.56	21.5	40.88	40.6
$(\mathrm{2,5\text{-}diMepyrCH_3^+})_n\{\mathrm{NiCl_3}\}_n$	pale yellow	155	252s,200m		20.36	19.5	36.89	36.3
$(\mathrm{2,6\text{-}diMepyrCH_3^+})_2[\mathrm{NiI_4}]$	burgundy	120			7.22	6.8	62.46	61.9

[a] For abbreviations, see Table I. [b] Compounds generally decomposed upon melting. [c] s = strong, m = medium, w = weak.

TABLE III. Electronic (d–d) Absorption Spectra of Co(II), Ni(II), and Cu(II) Complexes Containing N-Methylpyrazinium and N(1)-Methyl-2,5-dimethylpyrazinium Ligands.

Complex[a]	Absorption maxima[b], nm ($cm^{-1} \times 10^3$)		
Co(II), pseudo-tetrahedral (C_{3v})[c]	$^4E, ^4A_2\ (T_1, P)$	$^4E\ (T_1, F)$	$\leftarrow ^4A_2\ (F)$
$[\mathrm{CoCl_3(py\overset{+}{r}CH_3)}]$	606 (16.5)	1250 (8.00)	
$[\mathrm{CoBr_3(py\overset{+}{r}CH_3)}]$	638 (15.7)	1368 (7.30)	
$[\mathrm{CoCl_3(2,5\text{-}diMepy\overset{+}{r}CH_3)}]$	630 (15.9)	1300 (7.69)	
$[\mathrm{CoBr_3(2,5\text{-}diMepy\overset{+}{r}CH_3)}]$	668 (15.0)	1418 (7.05)	
Ni(II), trans-octahedral (D_{4h})[d]	$^3A_{2g}, ^3E_g\ (P)$	$^3A_2; ^3E_g\ (F)$	$^3B_{2g}, ^3E_g \leftarrow ^3B_{1g}$
$[\mathrm{NiCl_4(py\overset{+}{r}CH_3)_2}]$	450(22.2)	860(11.6)	1342(7.45)
$[\mathrm{NiBr_4(py\overset{+}{r}CH_3)_2}]$	450 (22.2)	884 (11.3)	1412 (7.08)
Cu(II), pseudo-tetrahedral	$^2E\ (^2T_2) \leftarrow ^2E$		
$[\mathrm{CuCl_3(py\overset{+}{r}CH_3)}]$	900 (11.1)		

[a] For abbreviations, see Table I. [b] From diffuse reflectance spectra. [c] Assignments follow reference 35. [d] Assignments follow reference 30.

and energies of the d–d absorptions are nearly identical to those of previously reported pseudo-tetrahedral (C_{3v}) complexes of the type $[CoX_3N]$, in which X is Cl or Br and N is the donor atom of a cationic aliphatic amine. The d–d spectrum of the $[CuCl_3(L^+)]$ complex is also consistent with a pseudo-tetrahedral environment of the metal ion. It should be noted that the spectra of these complexes exhibit very intense charge transfer absorptions in the near ultraviolet; these absorptions tail into the visible region and thus modify the typical colors of the tetrahedral metal ions.

All complexes have identical infrared patterns in the region 4000–350 cm^{-1}; these patterns resemble that of N-methylpyrazinium iodide in their general features, although differing in many details. In the lower energy region (350–200 cm^{-1}), the metal-halogen stretching modes appear as strong absorptions (Table I) with frequencies characteristic of tetrahedrally coordinated M(II) ion; these absorptions exhibit the splitting often observed for pseudo-tetrahedral MX_3 moieties [25, 28].

Taken together, the electronic and infrared spectra show that in these $MX_2 \cdot (L^+X^-)$ species the N-methylpyrazinium cation is coordinated to the metal ion, giving rise to a four-coordinate, pseudotetrahedral (C_{3v}) zwitterionic entity of the type $[MX_3(L^+)]$. The fact that the Co(II) and Zn(II) compounds form mixed crystals, $[(Co,Zn)X_3(L^+)]$, having the same electronic spectrum as the pure $[CoX_3(L^+)]$, further confirms the isostructural character of the compounds of this series.

The $[MX_3(L^+)]$ complexes of N-methylpyrazinium are thermally stable in the crystalline state and are insensitive to atmosphere moisture. They are readily soluble in polar solvents but undergo extensive decomposition. For example, the Co(II) complexes dissolved in dimethylformamide or nitromethane have electronic spectra nearly identical to those of the parent Co(II) halides in the same solvents. In nonpolar solvents, the $[MX_3(L^+)]$ complexes are quite insoluble, a feature commonly encountered in other compounds of this type [1–13] and related to their zwitterionic structure.

Compounds Containing Two N-methylpyrazinium Cations per Metal Ion

Some of the metal halides investigated in this work combine with the corresponding N-methylpyrazinium halides to produce compounds of the general formula $MX_2 \cdot 2(L^+X^-)$. The formulas, colors, melting points, and analytical data of the Ni(II) compounds are listed in Table I; those of the other compounds are collected in Table II, together with the room temperature magnetic moments of some representative species. The $MX_2 \cdot 2(L^+X^-)$ compounds correspond to two different structural types, involving in turn free and coordinated N-methylpyrazinium.

The Tetrahalometallate Salts

The $MX_2 \cdot 2(L^+X^-)$ species, in which X = Br for M = Cu(II) and X = I for M = Co(II) or Zn(II), have infrared spectra nearly identical to N-methylpyrazinium iodide, except for the presence of strong metal-halide absorptions characteristic of the corresponding tetrahalometallate ions. Also, the d–d electronic spectra of the $CoI_2 \cdot 2(L^+I^-)$ and $CuBr_2 \cdot 2(L^+Br^-)$ species are identical to those of the $[CoI_4^=]$ and $[CuBr_4^=]$ ions, respectively [29]. Accordingly, the compounds of this series are formulated as the tetrahalometallates of the uncoordinated N-methylpyrazinium cation. The magnetic moments measured for some of these complexes further support this formulation.

The tetrahalometallates of the N-methylpyrazinium cation are well-crystallized solids, which appear as small feathery platelets. They are thermally less stable than the corresponding zwitterionic complexes and also more sensitive to atmospheric moisture. Unlike the corresponding zwitterionic species, the $(L^+)_2[MX_4]$ salts are considerably soluble in organic solvents and may be recrystallized without decomposition from hot anhydrous ethanol containing a small excess of anhydrous metal halide.

The Octahedral Ni(II) Complexes

The Ni(II) compounds having the general formula $MX_2 \cdot 2(L^+X^-)$ appear as heavy micro-crystalline powders, mustard-yellow for the chloride and rust-colored for the bromide. Their d–d electronic spectra are clearly diagnostic of Ni(II) in an essentially octahedral environment and closely resemble those of previously reported complexes of the formula $[NiX_4(L^+)_2]$, in which L^+ is the trimethylhydrazinium cation-ligand, $[NH_2{-}N^+(CH_3)_3]$ [13]. The best fit between the observed spectra and the ligand field diagrams of König and Kremer [30] for d^8 systems in tetragonal symmetry are obtained for $D_q \cong 750$ cm^{-1}, $-100\ cm^{-1} > dt > -200\ cm^{-1}$, and K = 1. With these approximate values as guidelines and using Lever's method [32], the following values are obtained for the chlorocomplex: Dq (Cl, equatorial) = 610 cm^{-1}, Dq (N, axial) = 1000 cm^{-1}; Dt = –150 cm^{-1}. These values agree extremely well with those reported [32] for a number of halogen-bridged $[NiX_4N_2]$ chromophores. In particular, the complex $\{NiCl_2(py)_2\}_n$ has been assigned the following parameters: Dq (Cl, equatorial) = 600 cm^{-1}, Dq (N, axial) = 1080 cm^{-1}.

The infrared spectra of the complexes further confirm their formulation as *trans*-$[NiX_4(L^+)_2]$ species. In particular, the Ni-halogen stretching modes appear as a single strong band in the 200–250 cm^{-1} range, as expected for octahedrally coordinated Ni(II) in D_{4h} symmetry. Also, the absorption patterns of the organic moieties are quite simple and closely resemble those of the 1:1 zwitterionic species, indicating a symmetrical structure in which the two ligands are essentially independent of each other.

The *trans*-$[NiX_4(L^+)_2]$ complexes of the N-methylpyrazinium ligand are insoluble in most organic solvents and decompose when dissolved in water. When exposed to moist air, they absorb a small amount of water (1–3%), much less than required for the formation of stoichiometric 1:1 adducts. The uptake of moisture is accompanied by a slight color change resulting from variations in the shapes of the d–d and charge transfer absorptions without shifts in the band maxima; absorptions characteristic of weakly bound water also appear in the infrared spectrum. The addition of water to the $[NiX_4(L^+)_2]$ complexes is reversible and the original anhydrous species are reformed upon mild heating.

Compounds Containing N(1)-methyl-2,5-dimethylpyrazinium

The halides of this mono-hindered cation-ligand combine with the halides of a selected number of metal ions to produce crystalline compounds whose formulas, colors, melting points, and analytical data are listed in Tables I and II. Their structural identification closely parallels that of the N-methylpyrazinium derivatives.

The zwitterionic complexes of the type $[MX_3(L^+)]$ are well-crystallized, thermally stable solids, somewhat more sensitive to moisture than their unhindered N-methylpyrazinium analogs. The electronic spectra of the Co(II) complexes indicate a pseudotetrahedral geometry with C_{3v} symmetry, confirmed by the frequencies of the Co-halide stretching modes. A similar geometry is assigned to the Zn(II) complexes based on infrared spectra and on the formation of mixed (Co, Zn) crystals having electronic spectra identical with those of the pure Co(II) species. With Ni(II) chloride, a grayish-yellow powdery solid is obtained, of analytical composition corresponding to $NiCl_2 \cdot (L^+Cl^-)$. The infrared spectrum of this compound shows the characteristic pattern of the uncoordinated ligand as well as a strong Ni–Cl absorption at 252 cm^{-1}, in the region typical of octahedrally coordinated Ni(II). The electronic spectrum has a distinctive octahedral pattern and the band energies identify the chromophore as the well-known polymeric $\{NiCl_3^-\}_n$ ion [13, 32]. Accordingly, the $NiCl_2 \cdot (L^+Cl^-)$ compound may be formulated as a salt of formula $(L^+)_n\{NiCl_3^-\}_n$. The visible tail of a strong ultraviolet absorption is responsible for the color difference between this compound and the usual (light pink) $\{NiCl_3^-\}_n$ ion.

Reaction of Ni(II) Iodide with the Iodide of N(1)-methyl-2,6-dimethylpyrazinium

It has been shown [33] that doubly hindered pyridine ligands (*e.g.* 2,6-dimethylpyridine) can coordinate to metal ions under appropriate conditions and do so most readily with those metal ions, such as Ni(II) or Pd(II), which can assume an electronically favorable *trans*-$[MX_2L_2]$ geometry. It has also been observed that the highly polarizable I^- ligand markedly favors the formation of these compounds for the Ni(II) ion. With these premises, Ni(II) iodide appeared to be a likely acceptor for the doubly hindered N-methyl-2,6-dimethyl-pyrazinium cation and we attempted to obtain complexes under a variety of conditions. Only one product was isolated from these attempts—a red-brown crystalline solid of composition $NiI_2 \cdot 2(L^+I^-)$. From its infrared and electronic spectra this product was identified as the tetraiodonickelate(II) of the uncoordinated organic cation.

Conclusions

The N-methyl-pyrazinium cation can play a dual role with respect to divalent transition metal ions. In the presence of a large excess of metal halide, it usually behaves as a ligand, giving rise to zwitterionic complexes of two types—the pseudotetrahedral $[MX_3(L^+)]$ species, where M is Co(II), Cu(II), or Zn(II), and the *trans*-octahedral $[NiX_4(L^+)_2]$. If, however, the reaction system contains an excess of ligand halide or a high concentration of halide ions from other sources, the N-methyl-pyrazinium usually acts as a positive counterion and is precipitated as a halometallate salt. Steric hindrance also has a marked influence on the behavior of the pyrazinium cation-ligands: the unhindered species form both 2:1 and 1:1 complexes, the mono-hindered 2,5-dimethyl-derivatives form only 1:1 complexes, and the doubly hindered 2,6-dimethyl-derivative acts as a counterion.

The ease with which complexes of N-methylpyrazinium are obtained and their relatively high resistance to decomposition by solvents and atmospheric moisture show that there is no parallel between the coordinating ability of this cation-ligand toward metal ions and its tendency to bind protons. The lack of proton basicity actually appears to have a rather favorable effect on the formation and stability of the metal complexes of the monoquaternized pyrazinium cations, for it prevents the hydrolytic processes which often hinder the coordination of more basic amines [25, 33, 34].

It is instructive to compare the d–d electronic spectra of the zwitterionic Co(II) complexes of pyrazinium ligands with those of other $[CoX_3L]$ species of similar geometry; Table IV summarizes the absorption energies for some representative chloro-complexes. From the energy of the $^4A_2$ (F) → ^4E (T_1, F) transition, which is especially sensitive [35] to the difference in field strengths between the heteroligand (L^+ or L) and the accompanying halides (X), it may be concluded that the N-methylpyrazinium produces a field somewhat higher than that of cationic aliphatic amines or sterically hindered pyridines and approaching that of cationic aromatic phosphines [36]. Similar conclusions may be reached from the electronic spectra of the Ni(II) species, $[NiX_4(L^+)_2]$. These spectral features indicate that the coordination of the monoquaternized pyrazinium ligands must involve extensive π-electron delocalization from the metal ion into the available antibonding orbitals of the heteroaromatic ring, even when the electronic state of the metal itself is not particularly suited to π-back-bonding. In this respect, therefore, the mono-quaternized pyrazinium ligands closely resemble the uncharged parent pyrazines. For the monoquaternized ligands, however, π-back-bonding is necessarily restricted to the one-metal-one-ligand system of each zwitterionic entity, and thus can indeed be considered a feature typical of the individual metal-ligand link. This conclusion is supported by a recent report that N-methylpyrazinium forms a stable mononuclear adduct with the $[Co(CN)_5]^{3-}$ ion, a well-known acceptor for π-bonding ligands [37].

The present work points out that the monoquaternized pyrazinium cations possess a combination of characteristics—poor σ-donor and good π-acceptor ability, small size of the donor atom, compact and rigidly flat shape, lack of basicity toward protons—which is unique among water

TABLE IV. d–d Electronic Spectra of Some Pseudotetrahedral [$CoCl_3L$] Species.

Species[a]	Absorption maxima, nm ($cm^{-1} \times 10^3$)		
	$^4E, ^4A_2$ (T_1, P)	^4E (T_1, F) $^4A_2$ (F)	Reference
[$CoCl_3(pyrCH_3^+)$]	606 (16.5)	1,250 (8.00)	This work
[$CoCl_3$(2,5-diMepyrCH_3^+)]	630 (15.9)	1,300 (7.69)	This work
[$CoCl_3(PPh_3)]^-$	(not quoted)	1,250 (8.00)	[38]
[$CoCl_3(Ph_2PCH_2P^+Ph_2R)$]	662 (15.1)	1,220 (8.20)	[36]
[$CoCl_3(Ph_2PCH_2CH_2P^+Ph_2R)$]	684 (14.6)	1,282 (7.80)	[36]
[$CoCl_3(DABCOCH_3^+)$][b]	629 (15.9)	1,303 (7.67)	[3]
[$CoCl_3$(2,6-diMepy)]$^-$ [c]	630 (15.9)	1,450 (6.90)	[25]

[a] For abbreviations, see Table I. [b] $DABCOCH_3^+$ = 1-Methyl-1,4-diaza[2.2.2]bicyclooctonium cation. [c] 2,6-Dimethylpyridine.

soluble ligands. The monoquaternized pyrazinium cations should therefore prove especially useful in the study of those macrocyclic metal complexes in which axial interactions with nitrogenous bases subtly modify the reactivity and especially the electron-transfer properties of the system.

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