Contribution from the Department of Chemistry, The Florida State University, Tallahassee, Florida 32306, U.S.A.

Cation Ligands - The Donor Properties of the Monoprotonated 1,4-dimethylpiperazinium(+1) Cation

W.D. Perry, J.V. Quagliano, and L.M. Vallarino*

Received January 18, 1972

The ability of the monoprotonated 1,4-dimethylpiperazinium cation, L^+, to act as a ligand toward Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, is reported. The resulting zwitterion complexes $[MX_3(L^+)]$ (X = halide), are assigned a pseudotetrahedral geometry on the basis of their magnetic properties and d-d *electronic and infrared spectra.*

The unusually sharp $\overset{+}{N}$–H stretching absorption of these complexes suggests a highly ordered crystalline structure, with the protonated moiety of the coordinated ligand effectively free from hydrogen bonding. The donor ability of the L^+ ligands is discussed in comparison to that of other positively charged tertiary N-donor ligands.

Introduction

In our studies of the donor properties of positively charged tertiary N-donor ligands we first investigated[1-3] metal complexes of cation-ligands formed by monoquaternization of the "cage-like" ditertiary amine DABCO (I, Figure 1), and then extended our consideration to flexible-ring ligands such as those obtained by monoquaternization of 1,4-dimethylpiperazine.[4] In a preceding paper of this series we have described a number of metal complexes of the 1,1,4-trimethylpiperazinium(+1) cation (II, Figure 1), and compared its general coordinating ability with that of the DABCO-nium cation-ligands.[4] We now report the reaction between the halides of monoprotonated 1,4-dimethylpiperazine, (III, Figure 1), and the halides of the d^5 to d^{10} metal ions, Mn^{II} through Zn^{II}, except for Fe^{II}, which are known to have closely related acceptor properties.

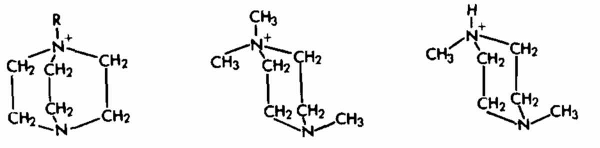
I II III

Figure 1. I, mono-quaternized DABCO-nium; II, 1,1,4-trimethylpiperazinium; III, monoprotonated 1,4-dimethylpiperazinium.

This work was undertaken because our previous investigations had shown that the type of metal complex formed with DABCO-nium ligands was markedly influenced by the nature of the quaternizing group.[3] It had not been possible to establish, however, whether the quaternizing group affects the coordination properties by indirect electronic interaction with the N-donor atom—interaction made possible by the unusually short nitrogen-nitrogen distance in DABCO[5,6]—or by direct electrostatic or steric interaction with neighboring groups in the crystal lattice. For protonated DABCO, moreover, hydrogen bonding of the $\overset{+}{N}$–H moiety to adjacent halo-ligands could also be considered an important factor. In the cation-ligands obtained by monoquaternization of 1,4-dimethylpiperazine, on the other hand, the flexible ring conformation should effectively reduce the interaction between the donor and quaternized N-atoms, and a meaningful comparison of the direct effects of different quaternizing groups—for example, methyl versus proton, should become possible.

Experimental Section

Preparation of Ligands. The 1,4-dimethylpiperazinium(+) chloride, bromide, and iodide, $[(CH_3)HN^+(CH_2CH_2)_2NCH_3]X$, (X = Cl, Br, I) were prepared by the dropwise addition of the halogen acid, diluted in acetone, to a chilled (0°C) and stirred acetone solution of 1,4-dimethylpiperazine (mole ratio 1:1). The colorless precipitates which immediately formed were filtered, washed with acetone and then with diethylether, and recrystallized from hot ethanol.

Anal. Calcd. for $C_6H_{15}N_2Cl$: Cl, 23.56; N, 18.56. Found: Cl, 23.4; N, 18.3. Calcd. for $C_6H_{15}N_2Br$: Br, 40.95; N, 14.35. Found: Br, 41.0; N. 14.0 Calcd. for $C_6H_{15}N_2I$: I, 52.41; N, 11.56. Found: I, 52.0; N, 11.1.

Preparation of Complexes $[MX_3(L^+)]$. $[CoCl_3(L^+)]$, $[CoBr_3(L^+)]$ $[CoI_3(L^+)]$, $[NiBr_3(L^+)]$, $[CuCl_3(L^+)]$, $[ZnCl_3(L^+)]$, $[ZnBr_3(L^+)]$, and $[ZnI_3(L^+)]$.

---

(1) J.V. Quagliano, A.K. Banerjee, V.L. Goedken, and L.M. Vallarino, *J. Am. Chem. Soc.*, *92*, 482 (1970).
(2) V.L. Goedken, J.V. Quagliano, and L.M. Vallarino, *Inorg. Chem.*, *8*, 2331 (1969).
(3) L.M. Vallarino, V.L. Goedken, and J.V. Quagliano, *Inorg. Chem.*, *12*, 102 (1973), and references therein.
(4) A.S.N. Murthy, J.V. Quagliano, and L.M. Vallarino. *Inorg. Chim. Acta*, *6*, 49 (1972).
(5) T. Wada, E. Kishida, Y. Tomhc, H. Suga, S. Seki, and I. Kitta, *Bull. Chem. Soc. Japan*, 33 1313 (1960).
(6) G.S. Weiss, A.S. Parker, E.R. Nixon, and R.E. Huges, *J. Chem. Phys.*, *41*, 3759 (1964).

Table I. Analytical Data and Some Properties of Compounds With The Monoprotonated 1,4-dimethylpiperazinium Cation-Ligand, L^+, and the Related Diprotonated Cation, LH^{2+}.

Complex	Color	Magnetic Moment μ_{eff}(B.M.)	$\nu(\overset{+}{N}-H)$ (cm^{-1})	% Metal		% Halide	
				Calcd.	Found	Calcd.	Found
$[NiCl_3(L^+)]$	blue	3.55	3086	20.93	20.9	37.98	37.9
$[NiBr_3(L^+)]$	blue	3.50	3080	14.19	14.1	57.95	57.8
$[CoCl_3(L^+)]$	blue	4.63	3108	20.99	21.0	37.95	38.0
$[CoBr_3(L^+)]$	blue	4.65	3095	13.99	14.2	57.93	57.9
$[CoI_3(L^+)]$	green	4.47	3085	10.62	10.9	68.62	68.5
$[CuCl_3(L^+)]$	yellow	1.96	3060	22.27	22.4	37.34	37.0
$[CuBr_3(L^+)]$	dark-brown	2.0	3046	15.18	15.0	57.29	56.9
$[ZnCl_3(L^+)]$	white	dia.	3108	22.78	22.7	37.10	36.9
$[ZnBr_3(L^+)]$	white	dia.	3100	15.56	15.7	57.03	57.1
$[ZnI_3(L^+)]$	white	dia.	3070	11.65	11.6	67.82	67.5
$(L^+)_2[MnCl_4]$	pale yellow	5.98	[a]	12.85	12.5	33.23	33.0
$(L^+)_2[MnBr_4]$	pale yellow-green	5.94	[a]	9.08	9.0	52.84	52.7
$(LH^{2+})[MnCl_4]$	white	5.97	[a]	17.53	17.2	45.35	45.2
$(LH^{2+})[MnBr_4]$	white	5.95	[a]	11.19	11.4	65.13	65.0
$(LH^{2+})[CuBr_4]$	dark-brown	1.93	[a]	12.72	12.8	64.01	63.5

[a] $(\overset{+}{N}-H)$ and (C—H) stretching modes overlap to give a broad intense absorption with many partly resolved peaks.

The ligands salts, $(L^+)X^-$, and the corresponding metal salts, MX_2, were separately dissolved in a mixture of 50% ethanol, 40% nitromethane and 10% triethylorthoformate. The solutions were boiled for a few minutes to facilitate removal of H_2O by triethylorthoformate, and the hot solution of the ligand halide was then added dropwise to the hot, stirred solution of the metal halide. In most cases the complexes precipitated immediately as crystalline powders. For $[CoI_3(L^+)]$ and $[NiBr_3(L^+)]$ however, the reaction mixture was heated just below boiling for 5-10 minutes before precipitation occurred. The complexes were filtered, washed repeatedly with small volumes of the solvent mixture, and dried *in vacuo*. In all cases pure compounds were obtained and analytical data are listed in Table I. The mole ratio of ligand to metal had little or no influence on the formation of these $[MX_3(L^+)]$ complexes. In fact, the same compound formed either with an excess of ligand or with an excess of metal, provided the solutions were rigorously anhydrous. All attempts to prepare a NiI_2 complex under similar conditions were unsuccessful.

$[NiCl_3(L^+)]$ and $[CuBr_3(L^+)]$. Solutions of the ligand halides and metal halides in 1:1 mixture of ethanol-nitromethane were dehydrated over 4A Linde Molecular Sieves for two days. The solution of the metal salt was then added dropwise to a stirred ligand solution with no heating. The powdery precipitates which formed after several minutes were filtered off, washed with absolute ethanol, and dried *in vacuo*. The $[NiCl_3(L^+)]$ complex is very hygroscopic. Attempts to prepare $[NiCl_3(L^+)]$ by a procedure similar to that outlined for $[NiBr_3(L^+)]$ gave instead the complex salts of the diprotonated cation: $(LH^{2+})_2Cl_2[NiCl_4(C_2H_5OH)]$ (purple), $(LH^{2+})_2Cl_2[NiCl_4(H_2O)_2]$ (yellow), and $(LH^{2+})_2Cl_2[NiCl_4]$ (blue). These compounds were previously prepared by using the chloride of diprotonated 1,4-dimethylpiperazine, LH^{2+}, as the starting material.[7]

$(L^+)_2[MnCl_4]$ and $(L^+)_2[MnBr_4]$ were prepared by the addition of Mn^{II} halide to the ligand halide, both in ethanol solution. The crystalline products were filtered, washed with ethanol, and dried *in vacuo*.

$(LH^{2+})[MnCl_4]$, $(LH^{2+})[MnBr_4]$, and $(LH^{2+})[CuBr_4]$ were obtained by the addition of the ligand halide to the metal halide, both in ethanol solution. (The ligand L^+ was protonated during the reaction to form the dipositive cation, LH^{2+}). Identical compounds were obtained by addition of the metal halides ot the halides of the dipositive cation, in ethanol solution.

Physical Characterization of the Complexes. The complexes were characterized by analyses, vibrational spectra (4000-250 cm^{-1}), *d-d* electronic spectra (30,000-4,000 cm^{-1}), and room temperature magnetic moments. Details of the procedures were given elsewhere.[4]

Results and Discussion

The reaction between the halides of the monoprotonated 1,4-dimethylpiperazinium(+1) cation, L^+, and the corresponding halides of some divalent metal ions —Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}—was investigated under a variety of experimental conditions. It was found that this positively charged ligand, L^+, behaves in essentially three different ways: (1) L^+ may coordinate to metal ions forming zwitterion complexes of the type $[MX_3(L^+)]$, where M is Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, and X is Cl, Br, and I; (2) L^+ may act as a simple counterion in tetrahalomanganate(II) salts, $(L^+)_2[MnX_4]$, where X is Cl or Br; (3) L^+ may take on an additional proton from solution, giving the dipositive cation, LH^{2+}, which acts as a counterion toward various complex metallate anions. It is convenient to discuss separately these different classes of compounds.

The Zwitterion Complexes $[MX_3(L^+)]$. The com-

---

(7) V.L. Goedken, L.M. Vallarino, and J.V. Quagliano, *J. Am. Chem. Soc.*, *92*, 303 (1970).

plexes of this type are listed in Table I, together with their colors, magnetic moments and analytical data. The complexes of Co^{II} and Ni^{II} have *d-d* electronic spectra and magnetic moments characteristic of these metal ions in a high-spin electron configuration and pseudo-tetrahedral stereochemistry. Furthermore, the marked splitting of the $^4A_2(F) \rightarrow {}^4T_1(F)$ transition in the Co^{II} complexes, and of the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition in the Ni^{II} complexes, indicates that the ligand field environment approaches a C_{3v} symmetry, consistent with coordination of one nitrogen atom and three halide ions.[8] These complexes, therefore, may be considered to have mononuclear zwitterion formulas, [CoX$_3$(L$^+$)] and [NiX$_3$(L$^+$)], similar to the corresponding complexes of other positively charged ligands, such as 1,1,4-trimethylpiperazinium(+1) and monoquaternized DABCO-nium.[1]

As previously observed for other flexible ring ligands, the infrared spectra of the complexes of monoprotonated 1 4-dimethylpiperazine are very sensitive to formula and geometry and can be used as a diagnostic tool. Thus, the Cu^{II} and Zn^{II} complexes which have infrared spectra virtually identical to those of the corresponding Co^{II} and Ni^{II} complexes, are also assigned a pseudo-tetrahedral zwitterion structure, [MX$_3$(L$^+$)], with C_{3v} symmetry. For all the chloro-complexes of this series, the metal-chlorine stretching vibrations appear as a strong, split band in the far infrared. The frequency values—ν, in cm^{-1}: 325, 304 for Co^{II}, 312, 293 for Ni^{II}; 320, 317 for Cu^{II}; 295, 288 for Zn^{II}—follow the general trend of the crystal field stabilization energies of these metal ions.

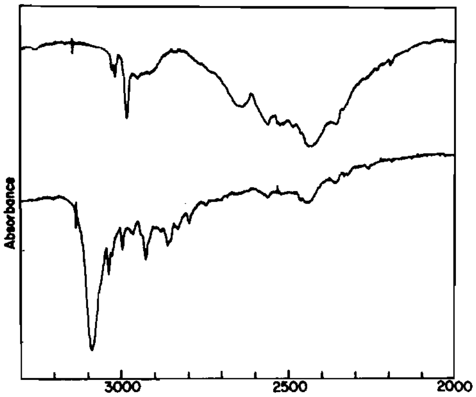

Figure 2. The ($N^{\pm}$–H) stretching absorption of monoprotonated 1,4-dimethylpiperazinium in the chloride salt (top line) and in the pseudotetrahedral complex [(NiCl$_3$(L$^+$)] (bottom line).

A significant feature in the infrared spectra of these [MX$_3$(L$^+$)] complexes is the unusually sharp, strong absorption at about 3100 cm^{-1}, (Figure 2), arising from the $N^{\pm}$–H stretching vibration. (In the "free" ligand halides, this absorption appears as an extremely broad, structured band, ranging from 3000 to 2200 cm^{-1}.) It can be noted that the $N^{\pm}$–H stretching frequency (Table I) varies only slightly with the metal ion and for each metal regularly decreases from the chloro- to the iodo-complex. Since the hydrogen bonding energy between a $N^{\pm}$–H group and halo-ligands would be expected to decrease greatly in the order Cl > Br > I, and ν($N^{\pm}$–H) would accordingly be expected to increase in the reverse order, the observed frequency trend leads to the rather surprising conclusion that the $N^{\pm}$–H group must not be involved in hydrogen-bonding. If we then assume, as is reasonable, that the [MX$_3$(L$^+$)] zwitterion complexes have a highly ordered crystalline structure, with the $N^{\pm}$–H groups all in the same environment and effectively isolated, the unique sharpness of the ν($N^{\pm}$–H) absorption becomes logically understandable, for the $N^{\pm}$–H group of the coordinated L$^+$ ligand essentially resembles the NH group of a neutral secondary amine in a non-hydrogen bonding solvent.

The Tetrahalometallate(II) Salts of the Monoprotonated and Diprotonated 1,4-Dimethylpiperazinium Cations. The reaction of Mn^{II} chloride and bromide with an excess of the corresponding halide of 1,4-dimethylpiperazinium yielded two white crystalline complexes of the simple formula MnCl$_2$ · 2(L$^+$)Cl and MnBr$_2$ · 2(L$^+$)Br. Since there is no convenient method to establish the stereochemistry of Mn^{II} complexes, an effort was made to prepare similar complexes of Co^{II} and/or Ni^{II}, which might be identified by their magnetic and *d-d* electronic spectral properties, and may then serve as a comparison for the Mn^{II} compounds. However, no complexes containing two L$^+$ ligands could be obtained with either Co^{II} or Ni^{II} which only form the zwitterion complexes, [MX$_3$(L$^+$)], even in the presence of a large excess of L$^+$ ligand. From the many analogies between the infrared spectra of the "free" ligand halides and those of the Mn^{II} complexes of simple formula MnX$_2$ · 2(L$^+$)X, these are tentatively formulated* as the tetrahalomanganates(II) of the "free" cation-ligand, (L$^+$)$_2$[MnCl$_4$] and (L$^+$)$_2$[MnBr$_4$].

In ethanol solutions of readily hydrolyzable metal salts, the monoprotonated ligand, L$^+$, may take on an additional proton to form the dipositive cation, CH$_3$(H)N$^+$(CH$_2$CH$_2$)$_2$N$^+$(H)CH$_3$, abbreviated as LH^{2+}, which is an excellent prepitating agent for divalent complex anions. For example, the reaction of monoprotonated 1,4-dimethylpiperazinium(+1) chloride with NiCl$_2$, under all but rigorously anhydrous conditions, gives the five-coordinate Ni^{II} complex salt (LH^{2+})$_2$Cl$_2$[NiCl$_4$(C$_2$H$_5$OH)], identical to that obtained from the diprotonated LH^{2+} cation as starting material. Protonation of the L$^+$ cation also occurs in solutions of Mn^{II} and Cu^{II} halides, especially when

---

[8] B.B. Garrett, V.L. Goedken, and J.V. Quagliano, *J. Am. Chem. Soc.*, *92*, 489 (1970).

* One of the referees has very kindly suggested that the stereochemistry of the Mn^{II} complexes can be determined from e.p.r. spectra of the powdered samples, as indicated for example by R.D. Dowsing, J.F. Gibson, M. Goodgame and P.J. Hayward, *J. Chem. Soc. A*, 1133 (1970). and references therein. We have therefore recorded the e.p.r. spectra of the Mn^{II} complexes reported in this paper together with those of many Mn^{II} compounds known to have six-coordinate octahedral, five-coordinate trigonal bipyramidal, and four-cordinate tetrahedral geometry. We find that the situation in regard to the e.p.r. « powder spectra » of various Mn^{II} complexes is more complicated than could have been anticipated from the rather limited data reported in the above reference and that much more information on this subject is needed before e.p.r. « powder spectra » can be used as a straightforward diagnostic method to establish the geometry of an unknown Mn^{II} complex.

Table II. d-d Electronic Spectra of the Crystalline Complexes $(MX_3(L^+)]$.

Complex	Absorption Maxima (kK) and Assignments [b]			
		$^4A_2(F)\rightarrow$		
	$^4A_2(T_1,F)$	$^4E(T_1,F)$		$^4E(T_1,P)$, $^4A_2(T_1,P)$
$[CoCl_3(L^+)]$	4.8 [c]	7.3		15.6
$[CoBr_3(L^+)]$	4.7 [c]	7.3, 6.4 [d]		15.4
$[CoI_3(L^+)]$	4.3 [c]	6.5		14.5
		$^3E(T_1,F)\rightarrow$		
	$^3E(T_2,F)$	$^3A_1(T_2,F)$	$^3A_2(F)$	$^3E(T_1,P)$, $^3A_2(T_1,P)$
$[NiCl_3(L^+)]$	4.7 [c]	6.1	8.9	16.3, 17.4
$[NiBr_3(L^+)]$	4.6 [c]	5.9	8.5	15.4, (16.3), (14.5) [e]

[a] $(L^+) = [CH_3N(CH_2CH_2)_2\overset{+}{N}(H)CH_3]$, monoprotonated 1,4-dimethylpiperazinium. [b] The reported values are midpoints of absorption bands of diffuse reflectance spectra. Assignments are made according to Ref. 8. [c] Partly overlaid by vibrational absorptions of the (L^+) ligand. [d] Poorly resolved splitting. [e] Parenthesis indicate shoulders.

the metal is in excess with respect to the ligand. The resulting complex salts, formulated as $(LH^{2+})[MnCl_4]$, $(LH^{2+})[MnBr_4]$, and $(LH^{2+})[CuBr_4]$, are identical to the compounds obtained by direct reaction of the diprotonated cation halides $(LH^{2+})X_2$ with solutions of Mn^{II} or Cu^{II} halides

Conclusions

The monoprotonated 1,4-dimethylpiperazinium(+1) cation coordinates to divalent transition metal ions via the tertiary N-donor atom, forming well-crystallized, stable zwitterion complexes of the type $[MX_3(L^+)]$. The ease with which these complexes can be obtained is remarkable when compared with the unusually poor donor properties of non-chelating tertiary N-donor ligands. In fact, to our knowledge no transition metal complexes of the tertiary amine, N-methylpiperidine $C_3N(CH_2CH_2)_2CH_2$—the uncharged analog of the positively charged ligand considered in this paper—have been reported in the literature. Also, attempts in this laboratory to prepare crystalline complexes of N-methylpiperidine with $CoCl_2$ and $NiCl_2$ have been unsuccessful. Thus the presence of the positive charge on the 1,4-dimethylpiperazinium(+1) cation-ligand undoubtedly favors the formation of its metal complexes, $[MX_3(L^+)]$, as previously discussed[4] for the related tertiary N-donor ligand, the 1,1,4-trimethylpiperazinium cation, II.

Perhaps the most significant result of the present work is that ligands II and III—which have the same coordination site, the same flexible-ring structure, and differ only in the quaternizing group—(a methyl versus a proton) also have virtually identical coordinating abilities. The only significant difference is that ligand III readily undergoes further protonation in ethanol solutions of Ni^{II} chloride, to form the five-coordinate complex salt, $(LH^{2+})_2Cl_2[NiCl_4(C_2H_5OH)]$, whereas ligand II forms only the zwitterion complex $[NiCl_3(L^+)]$. These different behaviors, however, may be considered to arise from slight differences in the hydrogen bonding abilities of the related dipositive cations, rather than from intrinsic differences of the ligands themselves. The unusual sharpness of the $N\overset{+}{-}H$ stretching absorption in the infrared spectra of the $[MX_3(L^+)]$ complexes of ligand III and its lack of sensitivity to the nature of the halide X, also indicates that the $N\overset{+}{-}H$ moiety is effectively isolated from the neighboring halo-ligands—that is, non-hydrogen bonded. In the complexes of ligand III hydrogen bonding should, therefore, be discounted as a possible stabilizing factor—a rather surprising conclusion which, however, fits in very well with the observed close similarity in behavior of the protonated and methylated ligands. It is reasonable to conclude that for these ligands the quaternizing group, whether protonated or methylated, does not have a direct effect on the type of complex formed, since the flxibility of the ring minimizes the electronic interactions between the quaternized and donor N-atoms, and also allows each complex species to assume the least-repulsive, most stable configuration. For the DABCO-nium ligands, on the other hand, the rigid cagelike structure allows a strong electronic interaction of the two N atoms, and the nature of the quaternizing group then indirectly determines the availability of the electron pair on the donor N-atom and hence the type of complex formed.

Acknowledgment. This investigation was supported by the National Science Foundation.