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Crystal and Molecular Structures of the Five-Coordinate Complexes [Ni(LCH₃)₂Cl₃]ClO₄ and [Cu(LCH₃)₂Cl₃]ClO₄, Where L⁺CH₃ = N-Methyl-1,4-diazabicyclo[2.2.2]octonium Ion

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The five-coordinate complex ions bis(N-methyl-1,4-diazabicyclo[2.2.2]octonium)trichloronickel(II) and -copper(II), in the form of their perchlorate salts, are isomorphous and isostructural and crystallize in the orthorhombic space group $Pbc2_1$ [C_{2v}; No. 27], with a = 13.059 (8), b = 12.529 (9) and c = 13.092 (8) Å for the nickel salt and a = 13.157 (8), b = 12.379 (8), and c = 13.117 (8) Å for the copper salt. Observed and calculated densities are 1.60 and 1.609 g cm⁻¹ for the nickel complex and 1.62 and 1.629 g cm⁻¹ for the copper complex for four molecules per unit cell. X-ray diffraction data in the range 2° < 2θ < 50° were collected for both salts on a Nonius CAD-3 diffractometer and the structures were solved via Patterson, Fourier, and least-squares methods. The final discrepancy indices, R and R_w for refinement based on F, are 0.053 and 0.081, respectively, for the 2063 independent reflections collected for the nickel complex and 0.090 and 0.092 for the 1989 independent reflections obtained for the copper analogue. The geometry of the five-coordination polyhedron for both salts is basically trigonal bipyramidal with small but significant angular deviations toward a polyhedron of C_{2v} symmetry. The equatorial Ni–Cl distances are shorter than the corresponding bonds in the copper complex, while the pattern is reversed for the axial M–N bond distances. The averaged distances are Ni–Cl = 2.300 (3), Cu–Cl = 2.349 (5), Ni–N = 2.226 (7), and Cu–N = 2.141 (14) Å. In addition to the angular deviations of the coordination polyhedra from D_{3h} symmetry observed in both complexes, for the nickel complex there is also a significant difference in Ni–Cl distances, the deviations being in accord with the C_{2v} geometry. Two of the bond lengths average 2.309 (3) Å while the third is 2.281 (3) Å. The bond length patterns are discussed in terms of the ground-state electronic structures of the two complexes and prevailing models of the stereochemistry of five-coordinate transition metal complexes. The complex cations pack together in a face-centered cubic close-packed array with the perchlorate ions occupying the octahedral holes in the structure.

Introduction

Five-coordinate complexes of the transition metals are now relatively common and detailed structural results are available for many of them.[1] Of interest from the viewpoint of electronic structure and the finer features of stereochemistry are the species containing unidentate ligands and especially those having five equivalent ligands. Discussion of structural features has revolved around two main points: the relative stability of square-pyramidal and trigonal-bipyramidal geometries for a given d-electron configuration and the equatorial–axial bond distance pattern for these two geometries. Clearly for such discussion, ML₅ species and series of ions forming complexes with the same group of ligands occupy a central role. Thus the pentacyano M(CN)₅³⁻ (M = Co,[2] Ni³) and pentachloro MCl₅ⁿ⁻ (M = Mn^{III},[4] Cu^{II},[5] Ni^{II},[6] Cd^{II 7}) complex ions fall into the first category while compounds of stoichiometry MX₃·2L where X is a halogen and L is a unidentate amine[8] or phosphine[9] belong to the second and have previously been the object of some study in our laboratory.[10] The series of complexes formed with the positively charged ligands L⁺H and L⁺CH₃ derived from 1,4-diazabicyclo[2.2.2]octane (Dabco) also belong to the second category and have been formulated as basically trigonal-bipyramidal complex ions, MCl₃(L⁺H)₂⁺ for M = Mn, Fe, Ni, and Cu and NiCl₃(L⁺CH₃)₂⁺, with the cationic amine ligands occupying the axial sites.[11] In terms of basic geometry these complexes offer the same feature for the later first-row ions, as is found in the trimethylamine complexes of the trihalides of Ti, V, and Cr, namely, the coordination of ligands with C₃ axes in the axial sites of a

trigonal bipyramid and the imposition of nearly threefold symmetry on the equatorial MX₃ group. In contrast to the MX₃·2NMe₃ complexes, however, the series of compounds formed with the Dabconium ligands are stable to hydrolysis and oxidation and offer the opportunity for single-crystal examination (polarized spectra, magnetic anisotropies, etc.) of electronic properties. For example, one of the controversial points regarding the electronic structure of five-coordinate copper complexes has concerned the relative d-orbital level ordering as determined from solution and mull spectra.[12,13] Unfortunately CuCl₅³⁻ belongs to the cubic system[5] so that its study in single-crystal form can shed no light on the problem.

In addition to examining the detailed changes in coordination geometry produced by the differing central metal ions, in the [MX₃(L⁺H)₂]⁺ complexes our purpose in carrying out the structure analyses therefore was also to obtain information on the orientation of the cations in the unit cell as a prelude to carrying out single-crystal susceptibility and spectroscopic studies. Unfortunately these studies have been thwarted in the case of nickel and copper complexes, [MCl₃(L⁺CH₃)₂]⁺, for the orientation of the cations in the pseudocubic unit cell precludes the possibility of obtaining any useful information on the anisotropy in their electronic properties from single-crystal measurements.

Experimental Section

Preparation of Complexes. The nickel complex was prepared in the manner described by Vallarino et al.[11] modified slightly to facilitate crystal growth. The red crystalline precipitate was washed with ethanol

and dried in vacuo. Anal. Calcd for $NiCl_4O_4N_4C_{14}H_{30}$: C, 32.28; H, 5.84; Cl, 27.33. Found: C, 32.33; H, 5.79; Cl, 27.04.

The copper complex, whose isolation has not previously been reported, was prepared in essentially the same manner as the nickel complex, except that to facilitate growth of reasonable crystals it was found necessary to add the $CuCl_2$ solution to the solution of $LiClO_4$ and $N(CH_2CH_2)_3N^+CH_3Cl^-$ over a period of several days. Anal. Calcd for $CuCl_4O_4N_4C_{14}H_{30}$: C, 32.08; H, 5.79; Cl, 27.08. Found: C, 31.84; H, 5.71; Cl, 27.15. All attempts to isolate the zinc complex by similar procedures were unsuccessful, and attempts to obtain suitable single crystals of complexes formed with the protonated ligand, L^+H, proved to be abortive.

Collection of X-Ray Diffraction Data. Crystals of both the nickel and copper complexes crystallize in the orthorhombic system with an octahedral habit, forms {111} being prominent. Photographic studies using Weissenberg and precession techniques gave approximate unit cell dimensions, showed *mmm* Laue symmetry, and indicated systematic absences $h0l$ for $l = 2n + 1$ and $0kl$ for $k = 2n + 1$. These absences are consistent with space groups $Pbcm$ [D_{2h}^{11}; No. 57] and $Pbc2_1$, an alternative setting for $Pca2_1$ [C_{2v}^5; No. 29]. The noncentrosymmetric space group was confirmed during the early stages of analysis. The setting used here has general equivalent positions: $x, y, z; -x, -y, \frac{1}{2} + z; x, \frac{1}{2} - y, \frac{1}{2} + z; -x, \frac{1}{2} + y, z$.

Well-formed crystals were used for intensity measurements which were performed on an Enraf-Nonius CAD-3 diffractometer. The crystals were aligned roughly along axial directions and unit cell dimensions were obtained by least-squares refinement of a number of high-angle reflections (26 for the Ni complex; 16 for the Cu complex) centered using the program SETANG.[14] The crystal faces were indexed and measured and absorption corrections were applied to the intensity data using a Gaussian integration method. The boundary planes and crystal dimensions are as follows. Nickel complex: {111}, 0.278 mm; {100}, 0.125 mm; {110}, 0.284 mm; crystal volume 0.0831 mm³. Copper complex: {111}, 0.176 mm (four faces); 0.201 mm (four faces); {100}, 0.150 mm; {100}, 0.200 mm; crystal volume 0.0406 mm³. Details of the data collection and experimental conditions are given in Table I.

Structure Solution and Refinement. Computations were carried out on a CDC 6600 computer using local modifications of Zalkin's FORDAP Fourier program, Prewitt's SFLS5 full-matrix least-squares routine, and various locally written programs. The neutral-atom scattering factors for all nonhydrogen atoms were taken from the tabulation by Cromer and Waber.[15] Anomalous dispersion corrections were not included. The hydrogen atom scattering factor used was that tabulated by Stewart.[16] The agreement factors are defined in the usual manner as $R = (\sum ||F_o| - |F_c||/(\sum |F_o|)$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum (F_o)^2]^{1/2}$, and in all least-squares refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, the weights being evaluated as $w^{1/2} = 2LpF_o/\sigma(I)$. Examination of a three-dimensional Patterson function calculated with the data for the nickel complex gave the coordinates for the metal atom and two of the chlorine atoms and indicated that the noncentrosymmetric space group was most probable ($Pbcm$ would require molecular C_s or C_i point symmetry). The agreement factors based on these coordinates were $R = 0.45$ and $R_w = 0.480$. The two remaining chlorine atoms and all nonhydrogen atoms were located in two Fourier syntheses and least-squares refinement of positional and isotropic thermal parameters led to $R = 0.116$ and $R_w = 0.118$ after two cycles. Two cycles of anisotropic refinement treating the complex cation in two parts to conserve computer costs gave $R = 0.066$ and $R_w = 0.094$. One complete cycle involved the refinement of one Dabconium ligand plus the $NiCl_3$ group and perchlorate ion followed by the refinement of the second ligand and the other groups.

Examination of a difference map yielded positions for approximately half of the ligand hydrogen atoms and these coordinates agreed well with those estimated using a C–H distance of 1.0 Å. Inclusion of all 30 independent hydrogens and refinement of their positional and isotropic thermal parameters gave $R = 0.059$ and $R_w = 0.081$. The calculated C–H distances varied from 0.74 to 1.35 Å while the B values had an unsatisfactorily large spread. The hydrogens were accordingly included as fixed contributions with B values given by the carbon to which they were attached. The anisotropic refinement then converged after two further cycles to $R = 0.054$ and $R_w = 0.081$. These values are based on all independent reflection data, those reflections for which $I(hkl) < 2\sigma(I)$ (170 in number) being given very low weight and being included in the refinement. The Δ/σ ratio was <0.3 for positional parameters and slightly higher for the thermal parameters. The

Table I. Experimental Data for X-Ray Diffraction Study

(A) Crystal Parameters at 21 °C

Ni complex	Cu complex
$a = 13.059$ (8) Å	$a = 13.157$ (8) Å
$b = 12.529$ (9) Å	$b = 12.379$ (9) Å
$c = 13.092$ (8) Å	$c = 13.117$ (8) Å
$V = 2142.1$ Å³	$V = 2136.4$ Å³
Mol wt 519.11	Mol 523.96
ρ(calcd) = 1.609 g cm⁻³	ρ(calcd) = 1.629 g cm⁻³
ρ(obsd) = 1.60 g cm⁻³	ρ(obsd) = 1.62 g cm⁻³

$Z = 4$, space group $Pbc2_1$ [C_{2v}^5; No. 29]

(B) Measurement of Intensity Data

Radiation: Mo Kα (Zr filter)
Attenuators: nickel foil; total of 5 used—factors (f) ranged from 1.26 to 12.10
Takeoff angle: 3.5°
Detector aperture: 1.2-mm diameter
Incident-beam collimator: 0.9-mm diameter
Crystal–detector distance: 98 mm
Crystal orientation: nickel complex aligned along [010]; copper complex, along [001]
Reflections measured: $+h,+k,+l$
Maximum 2θ: 50°
Scan type: coupled θ–2θ
Scan speed: 10°/min
Scan range: $\Delta(2\theta) = (1.0 + 0.20 \tan \theta)°$ centered about average peak position
Background measurement: stationary crystal, stationary counter; half scan time at beginning and end of 2θ scan
Standard reflection: one (045) measured every 50 reflections; no significant deviation from average
Reflections collected: Ni complex, 2063 independent measurements; Cu complex, 1989 independent measurements; each reflection scanned up to maximum of n_s times, number of scans (n_s) being determined by preset intensity; $n_s = 3$ (Ni complex); $n_s = 4$ (Cu complex)

(C) Treatment of Intensity Data

Conversion to I and $\sigma(I)$: $I = [P - (B_1 + B_2)](F/n_s)$ ($P = $ total count, $B = $ background); $\sigma(I) = [(P + B_1 + B_2)(F/n_s)^2 + (cI)^2]^{1/2}$; "ignorance factor" $c = 0.04$
Absorption coefficient: Ni complex, $\mu = 14.28$ cm⁻¹, max and min transmission factors 0.709 and 0.431; Cu complex, $\mu = 15.87$ cm⁻¹, max and min transmission factors 0.658 and 0.600

standard deviation of an observation of unit weight defined as $[\sum w[|F_o| - |F_c|]^2/(N_o - N_v)]^{1/2}$ had the rather high value of 2.08 indicating that the assigned deviations are probably underestimated.

As a starting point for the refinement of the data for the copper complex, the final positional parameters obtained for the nickel complex were used together with appropriate isotropic thermal parameters. On the basis of these input parameters, the agreement factors were $R = 0.166$ and $R_w = 0.175$. Further isotropic refinement was followed by two cycles of anisotropic refinement (again in block form) which led to $R = 0.096$ and $R_w = 0.104$. Inclusion of the hydrogen atoms as fixed contributions together with further refinement led to convergence with $R = 0.090$ and $R_w = 0.092$, these values again being for all 1989 independent reflections. Again all shifts in parameters in the final cycle were less than half the corresponding esd and the standard deviation in an observation of unit weight was 1.91. The ratio of observations to parameters was 8.5:1 for the nickel complex and 8.2:1 for the copper complex. Tables of observed and calculated structure factor amplitudes for both complexes are available[17] and positional parameters and their estimated standard deviations and anisotropic thermal parameters are collected together in Tables II–V.

Description and Discussion of the Structures

Tables VI–X contain pertinent structural information for the copper and nickel complex ions [MCl₃(L⁺CH₃)₂]⁺ with Table VI giving a comparison of the dimensions of the coordination polyhedra in the two complexes. Figure 1 gives a perspective view of the one complex ion and shows clearly the basically trigonal-bipyramidal geometry of the coordination polyhedron in these species.

Comparison of Coordination Polyhedra. Within the estimated standard deviations for the two structural determi-

Table II. Positional Parameters for [NiCl$_3$(N(CH$_2$CH$_2$)$_3$NCH$_3$)$_2$]ClO$_4$[a]

Atom	x	y	z
Ni	0.2459 (1)	0.0354 (1)	0.2500
Cl$_1$	0.1806 (3)	−0.0532 (2)	0.1125 (2)
Cl$_2$	0.3897 (2)	−0.0299 (2)	0.3302 (2)
Cl$_3$	0.1627 (2)	0.1879 (2)	0.3052 (2)
N$_1$	0.3462 (5)	0.1358 (5)	0.1528 (5)
N$_2$	0.1515 (5)	−0.0621 (6)	0.3575 (6)
N$_3$	0.4710 (5)	0.2462 (7)	0.0426 (6)
N$_4$	0.0410 (5)	−0.1731 (6)	0.4822 (5)
C$_1$	0.2878 (7)	0.1977 (8)	0.0766 (7)
C$_2$	0.4063 (7)	0.2121 (7)	0.2155 (6)
C$_3$	0.4195 (9)	0.0648 (7)	0.1014 (7)
C$_4$	0.3655 (8)	0.2470 (12)	0.0005 (10)
C$_5$	0.4673 (8)	0.2862 (9)	0.1473 (8)
C$_6$	0.5025 (9)	0.1278 (8)	0.0464 (9)
C$_7$	0.0403 (7)	−0.0470 (7)	0.3376 (8)
C$_8$	0.1771 (7)	−0.1765 (7)	0.3446 (8)
C$_9$	0.1722 (8)	−0.0280 (8)	0.4623 (7)
C$_{10}$	−0.0236 (6)	−0.0968 (7)	0.4168 (7)
C$_{11}$	0.0994 (7)	−0.2426 (7)	0.4089 (7)
C$_{12}$	0.1184 (7)	−0.1037 (8)	0.5371 (7)
C$_{13}$	0.5467 (8)	0.3062 (8)	−0.0231 (7)
C$_{14}$	−0.0193 (7)	−0.2406 (11)	0.5538 (8)
Cl$_4$	0.2797 (2)	0.5278 (2)	0.2676 (2)
O$_1$	0.2980 (11)	0.4843 (10)	0.1681 (8)
O$_2$	0.1752 (5)	0.5516 (8)	0.2849 (8)
O$_3$	0.3307 (8)	0.6252 (8)	0.2738 (11)
O$_4$	0.3185 (10)	0.4562 (9)	0.3412 (9)

[a] Standard deviations in parentheses.

Figure 1. Perspective view of the [MCl$_3$(L$^+$CH$_3$)$_2$]$^+$ ion—drawn using data for the nickel complex. The thermal ellipsoids are drawn at the 50% probability level.

nations the following features emerge when comparing dimensions: (a) the angular dispositions of the ligand around the central metal atoms are identical in both species; (b) the polyhedra deviate slightly from D_{3h} point symmetry and approximate more closely to C_{2v} with the M–Cl$_1$ bond being the twofold axis; (c) in the case of the nickel complex the Ni–Cl$_1$ distance differs significantly (by 9σ) from the average of the two remaining distances, while in the copper complex all metal–chlorine distances are equivalent; (d) the average M–Cl equatorial distance is significantly shorter (by 0.05 Å)

in the nickel complex than in the copper analogue, while the average M–N distance for the axial ligands is longer in the nickel complex (by 0.084 Å) than in the copper complex.

Examination of the least-squares plane information for the polyhedra given in Table VII suggests that the description in terms of a C_{2v} geometry is a reasonable one, for the best plane containing the axial nitrogens, N$_1$ and N$_2$, is that containing the chlorine atom, Cl$_1$, for both nickel and copper complex ions. In both complexes the N-methylDabconium ligands are bent away from Cl$_1$ by approximately 2° while the Cl$_2$–M–Cl$_3$ angle is increased from 120° by a comparable amount. These angular distortions are thus toward a square pyramid in which Cl$_1$ is the apical ligand.

The root-mean-square vibrational amplitude data for the atoms in the coordination sphere are listed in Table VIII, and as can be seen qualitatively from Figure 1, the motion of the equatorial chlorine atoms is quite anisotropic with the amplitude of vibration nearly in the equatorial plane and normal to the M–Cl bond, being appreciably larger than the other components. The angles between these major axes and the equatorial plane average 18° and suggest that the motion is primarily a libration of the complex around the pseudo-threefold axis.

The nickel–chlorine distances in the related complex containing one N-methylDabconium ligand, NiCl$_3$-(L$^+$CH$_3$)H$_2$O,[18] are 2.282 (2) and 2.339 (2) Å while the Ni–N distance of 2.140 (6) Å is significantly less than that observed

Table III. Thermal Parameters for [NiCl$_3$(N(CH$_2$CH$_2$)$_3$NCH$_3$)$_2$]ClO$_4$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0035 (1)	0.0038 (1)	0.0030 (1)	0.0004 (1)	−0.0005 (1)	−0.0001 (1)
Cl$_1$	0.0118 (3)	0.0082 (2)	0.0034 (1)	−0.0054 (2)	−0.0014 (2)	−0.0001 (1)
Cl$_2$	0.0038 (1)	0.0112 (2)	0.0065 (2)	0.0004 (1)	−0.0007 (1)	0.0051 (2)
Cl$_3$	0.0062 (2)	0.0042 (1)	0.0082 (2)	0.0082 (1)	0.0032 (1)	−0.0001 (1)
N$_1$	0.0042 (4)	0.0036 (5)	0.0023 (4)	0.0001 (3)	−0.0004 (3)	0.0000 (3)
N$_2$	0.0032 (4)	0.0039 (4)	0.0038 (4)	0.0006 (3)	0.0013 (3)	−0.0004 (4)
N$_3$	0.0048 (4)	0.0052 (5)	0.0039 (4)	0.0019 (4)	−0.0001 (3)	0.0002 (4)
N$_4$	0.0038 (4)	0.0051 (5)	0.0039 (4)	0.0007 (4)	−0.0011 (3)	−0.0000 (4)
C$_1$	0.0035 (5)	0.0059 (7)	0.0044 (5)	0.0000 (5)	−0.0006 (4)	0.0005 (5)
C$_2$	0.0051 (6)	0.0048 (6)	0.0031 (5)	−0.0006 (5)	0.0007 (4)	−0.0006 (4)
C$_3$	0.0081 (8)	0.0032 (5)	0.0043 (6)	0.0015 (6)	0.0002 (6)	−0.0007 (5)
C$_4$	0.0062 (6)	0.0085 (8)	0.0057 (6)	−0.0021 (8)	−0.0023 (7)	0.0035 (6)
C$_5$	0.0059 (6)	0.0086 (9)	0.0057 (6)	−0.0043 (6)	0.0017 (5)	−0.0024 (7)
C$_6$	0.0078 (8)	0.0057 (7)	0.0069 (7)	0.0030 (6)	0.0040 (7)	0.0019 (7)
C$_7$	0.0044 (5)	0.0052 (6)	0.0075 (7)	−0.0005 (5)	−0.0040 (5)	0.0003 (6)
C$_8$	0.0064 (6)	0.0042 (5)	0.0043 (6)	−0.0001 (5)	0.0002 (5)	0.0004 (5)
C$_9$	0.0058 (7)	0.0069 (7)	0.0037 (5)	−0.0020 (5)	−0.0009 (5)	0.0004 (5)
C$_{10}$	0.0034 (5)	0.0046 (6)	0.0052 (5)	0.0012 (4)	−0.0008 (4)	−0.0008 (5)
C$_{11}$	0.0054 (6)	0.0042 (6)	0.0045 (5)	−0.0003 (5)	0.0011 (5)	−0.0001 (5)
C$_{12}$	0.0054 (6)	0.0069 (5)	0.0044 (5)	−0.0016 (7)	0.0009 (5)	−0.0017 (5)
C$_{13}$	0.0056 (6)	0.0068 (7)	0.0042 (6)	−0.0010 (6)	−0.0012 (5)	0.0013 (5)
C$_{14}$	0.0047 (6)	0.0103 (8)	0.0048 (6)	−0.0031 (7)	0.0001 (5)	−0.0018 (6)
Cl$_4$	0.0045 (1)	0.0061 (2)	0.0044 (2)	0.0010 (1)	0.0001 (1)	0.0001 (1)
O$_1$	0.0154 (11)	0.0157 (11)	0.0056 (6)	0.0017 (9)	0.0011 (7)	−0.0003 (7)
O$_2$	0.0039 (4)	0.0158 (9)	0.0093 (8)	0.0006 (5)	0.0027 (5)	0.0013 (7)
O$_3$	0.0121 (8)	0.0103 (8)	0.0180 (14)	−0.0035 (7)	0.0017 (10)	−0.0001 (9)
O$_4$	0.0149 (11)	0.0131 (10)	0.0090 (8)	0.0046 (8)	0.0019 (7)	0.0039 (7)

[a] Standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Positional Parameters for
$[CuCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4{}^a$

Atom	x	y	z
Cu	0.2445 (1)	0.0364 (1)	0.2500
Cl_1	0.1770 (5)	−0.0558 (4)	0.1093 (4)
Cl_2	0.3892 (3)	−0.0325 (4)	0.3322 (4)
Cl_3	0.1623 (3)	0.1948 (3)	0.3051 (5)
N_1	0.3410 (9)	0.1315 (11)	0.1534 (9)
N_2	0.1528 (10)	−0.0572 (10)	0.3535 (11)
N_3	0.4661 (11)	0.2397 (13)	0.0439 (13)
N_4	0.0448 (10)	−0.1692 (11)	0.4834 (9)
C_1	0.2849 (13)	0.1971 (15)	0.0792 (14)
C_2	0.4034 (12)	0.2106 (14)	0.2177 (13)
C_3	0.4134 (15)	0.0602 (14)	0.0985 (13)
C_4	0.3583 (14)	0.2466 (20)	0.0030 (18)
C_5	0.4683 (14)	0.2816 (14)	0.1507 (15)
C_6	0.4960 (15)	0.1262 (14)	0.0474 (16)
C_7	0.0408 (11)	−0.0442 (13)	0.3331 (17)
C_8	0.1768 (12)	−0.1757 (12)	0.3468 (13)
C_9	0.1704 (13)	−0.0261 (14)	0.4593 (13)
C_{10}	−0.0184 (14)	−0.0939 (13)	0.4169 (14)
C_{11}	0.0996 (12)	−0.2426 (14)	0.4057 (14)
C_{12}	0.1216 (13)	−0.1036 (16)	0.5362 (16)
C_{13}	0.5389 (14)	0.2991 (16)	−0.0235 (16)
C_{14}	−0.0152 (13)	−0.2311 (15)	0.5543 (15)
Cl_4	0.2811 (3)	0.5309 (4)	0.2675 (4)
O_1	0.2945 (19)	0.4820 (19)	0.1718 (16)
O_2	0.1780 (10)	0.5579 (15)	0.2831 (14)
O_3	0.3311 (12)	0.6328 (12)	0.2732 (21)
O_4	0.3163 (17)	0.4581 (19)	0.3411 (16)

^{a} Standard deviations in parentheses.

here. In this complex, which has a crystallographically imposed mirror plane, the angular distortions from D_{3h} geometry toward a square pyramid are considerably larger than in $[NiCl_3(L^+CH_3)_2]^+$, but as in the latter, the apical nickel-chlorine distance (in the SP description) is shorter than the equatorial distance. The $NiCl_3$ grouping in the monoDab-conium complex is significantly nonplanar, the three chlorines being bent away from the axial Dabconium ligand, presumably to relieve steric repulsion. The angular distortions and difference in the Ni–Cl distances are attributed to hydrogen

bonding and electrostatic forces involving the quarternized nitrogen. A comparable distribution of distances is also found in the five-coordinate dimeric complex ion $Ni_2Cl_8{}^{4-}$, which is stabilized in the crystal by the $(HLCH_3)^{2+}$ ion.[6] The metal ion geometry is very close to square pyramidal with an apical distance of 2.283 (2) Å and the average of the two nonbridging equatorial distances being 2.354 (2) Å. The Cu–Cl distances in the copper complex average 2.349 (5) Å which is significantly shorter than the equatorial distance in the $CuCl_5{}^{3-}$ ion[5] but longer than the copper–chlorine distances in the dimeric $Cu_2Cl_8{}^{4-}$ ions, which contain distorted trigonal-bipyramidal copper.[14]

In terms of a simple repulsion model, the geometry of a five-coordinate transition metal complex can be considered the net result of valence-shell electron pair repulsions—causing axial bonds to be longer than equatorial bonds in the case of a trigonal-bipyramidal complex and the apical bond to be shorter than the basal bonds in a square pyramid—and the effect of interactions of the formally nonbonding d electrons with the valence-shell electrons.[1,20] A simple molecular orbital model considering only σ-bonding effects for the metal d orbitals leads to similar conclusions. In the case of trigonal-bipyramidal complexes the $a'_1(z^2)$ and $e'(xy, x^2 - y^2)$ orbitals will be predominantly antibonding while the $a'_1(z^2)$ and $b_1(x^2 - y^2)$ orbitals play the same role in the square-pyramidal geometry.[1]

Either model accounts satisfactorily for the observed geometries of $CuCl_5{}^{3-}$[5] and $Co(\alpha\text{-pic-}N\text{-O})_5{}^{2+}$,[21] the metal-carbon bond distance pattern in the square-pyramidal low-spin pentacyano complexes of nickel[3] and cobalt,[2] and the structures of other species which contain unidentate ligands and which have the relevant d orbitals partially or fully occupied.[1,22] From the results of the present analyses, which represent the first examples of monomeric nickel and copper five-coordinate complexes containing the same set of ligands, we see that the above models are appropriate in explaining points (c) and (d) (vide supra). The major difference between the two complex ions is the presence of an additional electron in the e' orbital of the copper complex (configuration $(e'')^4(e')^4(a')^1$) predicting

Table V. Thermal Parameters for $[CuCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4{}^a$

Atom	β_{11}	β_{12}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0032 (1)	0.0039 (1)	0.0025 (1)	0.0001 (1)	−0.0004 (1)	0.0000 (1)
Cl_1	0.0088 (4)	0.0071 (4)	0.0028 (3)	−0.0040 (4)	−0.0010 (3)	0.0005 (3)
Cl_2	0.0033 (2)	0.0106 (5)	0.0045 (3)	0.0009 (3)	−0.0001 (3)	0.0042 (4)
Cl_3	0.0051 (3)	0.0041 (3)	0.0060 (4)	0.0005 (3)	0.0022 (3)	−0.0005 (3)
N_1	0.0034 (9)	0.0040 (10)	0.0032 (9)	0.0006 (8)	0.0001 (8)	0.0008 (9)
N_2	0.0032 (9)	0.0037 (9)	0.0027 (10)	0.0003 (7)	−0.0036 (8)	0.0000 (9)
N_3	0.0050 (11)	0.0044 (10)	0.0041 (10)	0.0000 (10)	0.0002 (10)	0.0002 (10)
N_4	0.0034 (9)	0.0054 (11)	0.0038 (11)	0.0001 (8)	−0.0009 (8)	0.0005 (9)
C_1	0.0036 (11)	0.0053 (13)	0.0036 (12)	−0.0002 (11)	−0.0006 (10)	0.0002 (11)
C_2	0.0049 (10)	0.0058 (13)	0.0024 (10)	0.0004 (10)	−0.0005 (9)	−0.0017 (10)
C_3	0.0081 (15)	0.0046 (13)	0.0018 (11)	0.0020 (12)	0.0010 (11)	−0.0004 (11)
C_4	0.0064 (12)	0.0063 (13)	0.0049 (11)	−0.0027 (16)	−0.0012 (14)	0.0037 (11)
C_5	0.0050 (14)	0.0054 (14)	0.0038 (14)	−0.0024 (11)	0.0002 (11)	−0.0029 (13)
C_6	0.0054 (13)	0.0044 (13)	0.0056 (15)	0.0004 (11)	0.0046 (13)	−0.0006 (13)
C_7	0.0027 (9)	0.0043 (11)	0.0063 (14)	0.0009 (9)	−0.0006 (11)	−0.0021 (13)
C_8	0.0047 (11)	0.0039 (11)	0.0020 (10)	0.0005 (10)	−0.0004 (10)	0.0000 (10)
C_9	0.0045 (12)	0.0047 (13)	0.0025 (9)	−0.0002 (11)	−0.0012 (11)	0.0013 (11)
C_{10}	0.0038 (12)	0.0035 (12)	0.0051 (14)	−0.0004 (10)	0.0019 (11)	−0.0006 (11)
C_{11}	0.0049 (10)	0.0039 (11)	0.0033 (11)	−0.0001 (10)	0.0003 (10)	−0.0002 (11)
C_{12}	0.0048 (11)	0.0070 (16)	0.0043 (13)	−0.0004 (12)	0.0002 (12)	−0.0018 (14)
C_{13}	0.0049 (15)	0.0066 (15)	0.0048 (14)	−0.0014 (12)	0.0028 (13)	0.0011 (13)
C_{14}	0.0049 (13)	0.0047 (15)	0.0052 (13)	−0.0005 (13)	0.0017 (12)	0.0016 (12)
Cl_4	0.0043 (3)	0.0062 (3)	0.0039 (4)	0.0009 (3)	0.0000 (3)	0.0002 (3)
O_1	0.0169 (21)	0.0157 (21)	0.0062 (14)	0.0060 (17)	0.0004 (15)	−0.0022 (15)
O_2	0.0039 (8)	0.0191 (20)	0.0098 (17)	0.0017 (11)	0.0020 (10)	0.0003 (16)
O_3	0.0105 (13)	0.0096 (14)	0.0245 (29)	−0.0035 (12)	0.0026 (20)	−0.0035 (20)
O_4	0.0145 (21)	0.0170 (24)	0.0099 (19)	0.0031 (18)	−0.0012 (17)	0.0064 (18)

^{a} Standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
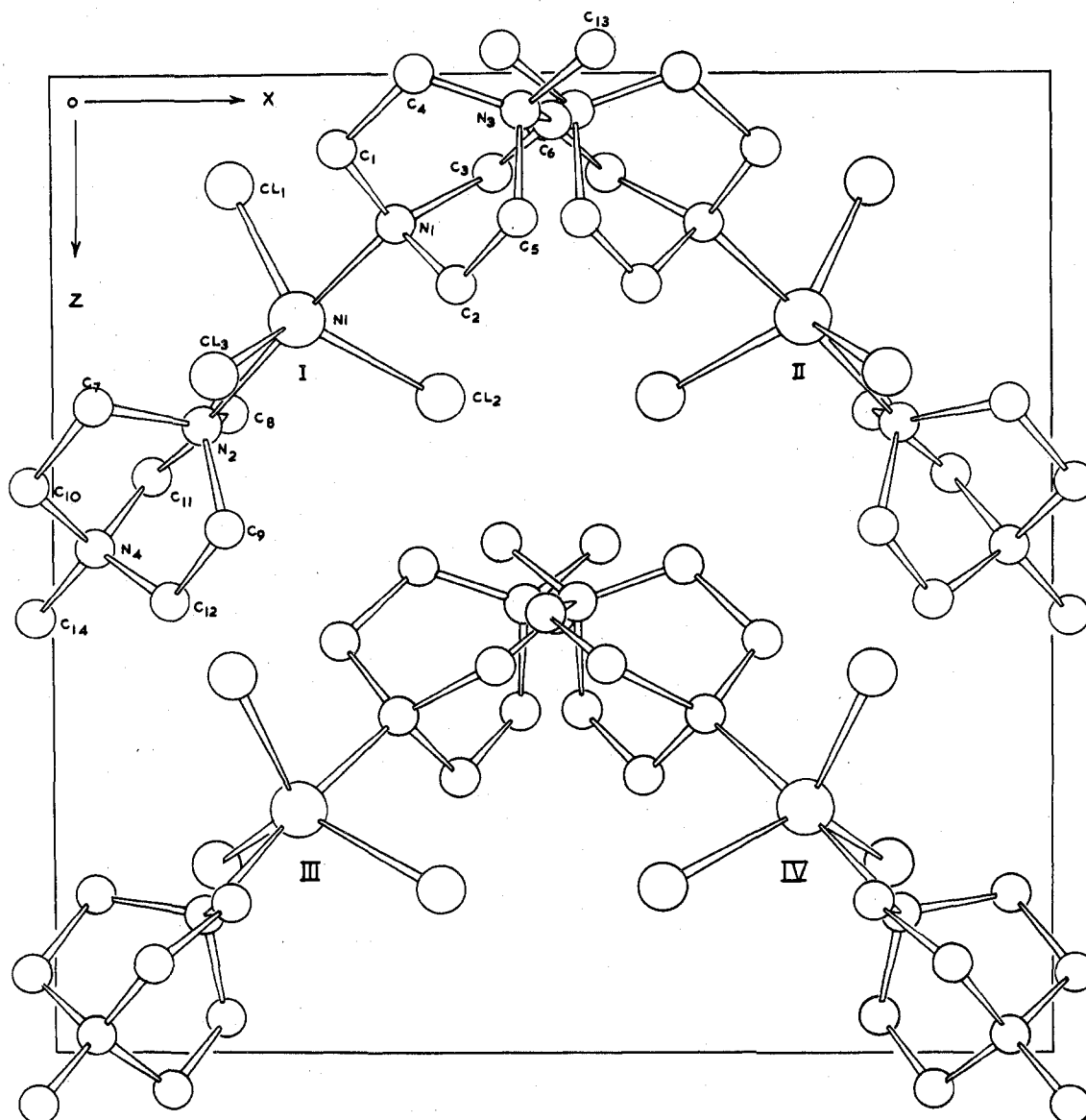
Figure 2. An [010] projection of the structure of $[MCl_3(L^+CH_3)_2]ClO_4$, omitting the perchlorate ions for clarity. The numbered atoms in the cation define the asymmetric unit.

Table VI. Comparison of the Geometry around the Metal Atom for $[MCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4$ (M = Ni, Cu)[a]

	M = Ni	M = Cu
Bond Distances, Å		
$M-Cl_1$	2.281 (3)	2.345 (6)
$M-Cl_2$	2.302 (3)	2.349 (5)
$M-Cl_3$	2.315 (3)	2.353 (5)
$M-N_1$	2.218 (7)	2.128 (13)
$M-N_2$	2.235 (7)	2.155 (14)
Bond Angles, Deg		
Cl_1-M-Cl_2	119.5 (1)	119.4 (2)
Cl_1-M-Cl_3	118.2 (1)	118.3 (2)
Cl_2-M-Cl_3	122.3 (1)	122.3 (2)
N_1-M-Cl_1	92.5 (2)	92.2 (4)
N_1-M-Cl_2	89.0 (2)	89.0 (4)
N_1-M-Cl_3	89.3 (2)	89.5 (4)
N_2-M-Cl_1	91.4 (2)	91.3 (4)
N_2-M-Cl_2	88.2 (2)	88.3 (4)
N_2-M-Cl_3	89.8 (2)	89.8 (4)
N_1-M-N_2	175.9 (2)	176.4 (5)

[a] Standard deviations in parentheses.

a longer Cu–Cl than Ni–Cl bond distance, which is in fact observed. The axial bond distances can then be rationalized

Table VII. Least-Squares Plane Data for the Coordination Polyhedra in $MCl_3(N(CH_2CH_2)_3NCH_3)_2^+$ (M = Ni, Cu)

Plane 1[a]

$-0.5739X - 0.5508Y + 0.6060Z - 0.0968 = 0$ (M = Ni)

Atom	Ni	Cl_1	Cl_2	Cl_3	N_1	N_2
Dist from plane, Å	−0.008	0.0036	0.0036	0.0028	−2.222	2.227

$-0.5811X - 0.5403Y + 0.6086Z - 0.1115 = 0$ (M = Cu)

Atom	Cu	Cl_1	Cl_2	Cl_3	N_1	N_2
Dist from plane, Å	−0.006	0.0035	0.0038	0.0032	−2.133	2.148

Plane 2

$-0.7348X - 0.6743Y + 0.0737Z + 2.304 = 0$ (M = Ni)

Atom	Ni	Cl_1	N_1	N_2
Dist from plane, Å	−0.002	−0.013	0.019	0.020

$0.7262X - 0.6829Y + 0.0792Z + 2.289 = 0$ (M = Cu)

Atom	Cu	Cl_1	N_1	N_2
Dist from plane, Å	−0.002	−0.013	0.019	0.021

[a] The form of the least-squares plane is $lX + mY + nZ + d = 0$ where X, Y, Z are orthogonal coordinates. The weights used were for the *i*th atom $w_i = 1/(a\sigma_x b\sigma_y c\sigma_z)^{2/3}$.

Table VIII. RMS Amplitudes of Vibration for Selected Atoms in $[MCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4$

Atom	Axes (M = Ni)			Axes (M = Cu)		
	Minor	Intermed	Major	Minor	Intermed	Major
M	0.151 (4)	0.167 (5)	0.184 (5)	0.142 (4)	0.171 (5)	0.175 (5)
Cl_1	0.161 (5)	0.205 (6)	0.351 (9)	0.151 (6)	0.178 (7)	0.320 (10)
Cl_2	0.167 (5)	0.201 (6)	0.382 (10)	0.135 (5)	0.174 (7)	0.319 (11)
Cl_3	0.165 (5)	0.202 (6)	0.289 (9)	0.156 (7)	0.191 (8)	0.261 (11)
N_1	0.150 (15)	0.175 (16)	0.180 (17)	0.148 (17)	0.168 (20)	0.196 (21)
N_2	0.126 (13)	0.184 (17)	0.201 (18)	0.121 (15)	0.170 (21)	0.221 (26)
Cl_4	0.184 (6)	0.195 (6)	0.232 (7)	0.182 (8)	0.186 (8)	0.228 (9)
O_1	0.218 (16)	0.339 (21)	0.380 (28)	0.215 (20)	0.302 (25)	0.432 (40)
O_2	0.155 (12)	0.295 (18)	0.359 (24)	0.166 (18)	0.300 (23)	0.388 (29)
O_3	0.248 (17)	0.346 (22)	0.402 (28)	0.229 (21)	0.320 (26)	0.475 (43)
O_4	0.234 (16)	0.296 (20)	0.411 (27)	0.213 (20)	0.357 (29)	0.415 (40)

Table IX. Ligand Bond Distances and Angles for $[NiCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4{}^a$

Bond Distances, Å

N_1-C_1	1.477 (11)	N_2-C_7	1.488 (11)
N_1-C_2	1.484 (11)	N_2-C_8	1.481 (11)
N_1-C_3	1.470 (12)	N_2-C_9	1.462 (12)
N_3-C_4	1.484 (13)	N_4-C_{10}	1.537 (11)
N_3-C_5	1.461 (13)	N_4-C_{11}	1.504 (11)
N_3-C_6	1.542 (13)	N_4-C_{12}	1.514 (12)
N_3-C_{13}	1.512 (13)	N_4-C_{14}	1.489 (13)
C_1-C_4	1.550 (15)	C_7-C_{10}	1.471 (13)
C_2-C_5	1.514 (14)	C_8-C_{11}	1.557 (13)
C_3-C_6	1.522 (15)	C_9-C_{12}	1.534 (14)

Bond Angles, Deg

C_1-N_1-Ni	112.4 (5)	C_7-N_2-Ni	111.0 (6)
C_2-N_1-Ni	111.1 (5)	C_8-N_2-Ni	109.4 (5)
C_3-N_1-Ni	107.7 (5)	C_9-N_2-Ni	109.3 (5)
$C_1-N_1-C_2$	107.9 (6)	$C_7-N_2-C_8$	108.8 (7)
$C_1-N_1-C_3$	110.2 (7)	$C_7-N_2-C_9$	107.9 (7)
$C_2-N_1-C_3$	107.4 (6)	$C_8-N_2-C_9$	110.4 (7)
$C_4-N_3-C_{13}$	113.1 (9)	$C_{10}-N_4-C_{14}$	114.4 (7)
$C_5-N_3-C_{13}$	112.7 (8)	$C_{11}-N_4-C_{14}$	110.0 (7)
$C_6-N_3-C_{13}$	108.9 (8)	$C_{12}-N_4-C_{14}$	112.4 (7)
$C_4-N_3-C_5$	108.4 (9)	$C_{10}-N_4-C_{11}$	106.5 (7)
$C_4-N_3-C_6$	105.4 (8)	$C_{10}-N_4-C_{12}$	105.9 (7)
$C_5-N_3-C_6$	108.0 (8)	$C_{11}-N_4-C_{12}$	107.3 (7)
$N_1-C_1-C_4$	107.8 (8)	$N_2-C_7-C_{10}$	112.2 (8)
$N_1-C_2-C_5$	110.3 (7)	$N_2-C_8-C_{11}$	107.8 (7)
$N_4-C_3-C_6$	111.5 (8)	$N_2-C_9-C_{12}$	109.5 (8)
$C_1-C_4-N_3$	111.5 (10)	$C_7-C_{10}-N_4$	110.2 (8)
$C_2-C_5-N_3$	111.2 (9)	$C_8-C_{11}-N_4$	111.6 (7)
$C_3-C_6-N_3$	109.0 (8)	$C_9-C_{12}-N_4$	110.9 (7)

^{a} Standard deviations in parentheses.

Table X. Ligand Bond Distances and Angles for $[CuCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4{}^a$

Bond Distances, Å

N_1-C_1	1.487 (22)	N_2-C_7	1.506 (20)
N_1-C_2	1.514 (21)	N_2-C_8	1.503 (20)
N_1-C_3	1.500 (22)	N_2-C_9	1.459 (23)
N_3-C_4	1.519 (23)	N_4-C_{10}	1.481 (23)
N_3-C_5	1.494 (25)	N_4-C_{11}	1.496 (23)
N_3-C_6	1.460 (24)	N_4-C_{12}	1.506 (24)
N_3-C_{13}	1.496 (25)	N_4-C_{14}	1.490 (24)
C_1-C_4	1.518 (27)	C_7-C_{10}	1.482 (26)
C_2-C_5	1.508 (25)	C_8-C_{11}	1.520 (23)
C_3-C_6	1.515 (27)	C_9-C_{12}	1.533 (26)

Bond Angles, Deg

C_1-N_1-Cu	113.4 (10)	C_7-N_2-Cu	112.2 (12)
C_2-N_1-Cu	111.7 (10)	C_8-N_2-Cu	111.7 (10)
C_3-N_1-Cu	110.2 (10)	C_9-N_2-Cu	111.6 (11)
$C_1-N_1-C_2$	106.2 (12)	$C_7-N_2-C_8$	107.4 (14)
$C_1-N_1-C_3$	107.3 (13)	$C_7-N_2-C_9$	107.2 (14)
$C_2-N_1-C_3$	107.8 (12)	$C_8-N_2-C_9$	106.3 (13)
$C_4-N_3-C_{13}$	111.2 (16)	$C_{10}-N_4-C_{14}$	112.9 (15)
$C_5-N_3-C_{13}$	111.8 (14)	$C_{11}-N_4-C_{14}$	111.7 (14)
$C_6-N_3-C_{13}$	108.6 (15)	$C_{12}-N_4-C_{14}$	106.8 (15)
$C_4-N_3-C_5$	109.2 (15)	$C_{10}-N_4-C_{11}$	108.2 (14)
$C_4-N_3-C_6$	108.4 (16)	$C_{10}-N_4-C_{12}$	108.2 (15)
$C_5-N_3-C_6$	107.5 (14)	$C_{11}-N_4-C_{12}$	109.0 (14)
$N_1-C_1-C_4$	110.4 (16)	$N_2-C_7-C_{10}$	109.8 (17)
$N_1-C_2-C_5$	111.8 (14)	$N_2-C_8-C_{11}$	111.2 (14)
$N_1-C_3-C_6$	111.1 (15)	$N_2-C_9-C_{12}$	113.2 (15)
$C_1-C_4-N_3$	109.8 (18)	$C_7-C_{10}-N_4$	111.4 (16)
$C_2-C_5-N_3$	109.5 (14)	$C_8-C_{11}-N_4$	108.2 (14)
$C_3-C_6-N_3$	109.9 (15)	$C_9-C_{12}-N_4$	106.5 (15)

^{a} Standard deviations in parentheses.

in this simple model in terms of the ligand–ligand repulsions, the longer Cu–Cl distance permitting a shorter metal–nitrogen bond in the copper complex than is found in the nickel analogue. The strongly antibonding $a'_1(z^2)$ orbital is singly occupied in both species. A similar pattern is observed in the complexes of the tetradentate amine Me_6tren,[23] the axial M–N distances being shorter than the equatorial bonds in the Ni^{2+} and Cu^{2+} species with the larger axial–equatorial difference being found in the latter.

The difference in the equatorial Ni–Cl distances can be attributed to the asymmetric electron distribution in the e' orbitals (configuration $(e'')^4(e')^3(a')^1$). The ground state for the d^8 high-spin configuration in D_{3h} geometry is $^3E'$, which according to the Jahn–Teller theorem should be unstable with respect to a distortion removing the threefold symmetry.[24] The observed shortening of one bond relative to the other two is in keeping with the simple bonding models for the high-spin d^8 configuration which predict that for a C_{2v} geometry (and, in the limit, a square pyramid) the apical bond distance (here Ni–Cl_1) will be shorter than the basal distances. Such a pattern is invariably found for high-spin square-pyramidal nickel complexes.[1b] It thus appears that the small angular distortions observed for both complexes are insufficient in the

case of the nickel complex to completely remove the orbital degeneracy predicted for a trigonal bipyramid.

Ligand Conformations and Molecular Packing. It can be seen from Figure 1 that the axial Dabconium ligands take up a staggered configuration with respect to the equatorial MCl_3^- groups, in a fashion similar to that of the trimethylamine groups in their adducts with the trihalides of Ti, V, Cr, etc.[8,10] The distances from the "unique" chlorine Cl_1 to the carbon atoms C_1, C_3, C_7, and C_8 average 3.455 (14) $Å^{25}$ in the nickel complex and 3.441 (18) Å in the copper complex while the four distances from chlorines Cl_2 and Cl_3 to carbons C_2 and C_9 average 3.381 (15) and 3.367 (18) Å in the two complexes. The deviations from the average in each case are not significant, so that the approximate C_{2v} symmetry also extends to the carbons C_1, C_2, C_3 and C_7, C_8, C_9.

Considering the complete ligands however, the individual rings take on a partial gauche conformation so that the potential symmetry of each Dabconium ligand is C_3 rather than C_{3v}. The average dihedral angle for the rings (six values per complex) is 14.0 (9)° for the nickel complex and 15.6 (10)° for the copper complex. A similar twist of ca. 14° about the threefold axis was observed in the cation in the structure of $[(HLCH_3{}^{2+})_2Ni_2Cl_8{}^{4-}]$,[6] so that it appears to arise from the

Table XI. Perchlorate Bond Distances and Angles for
$[MCl_3(N(CH_2CH_2)_3NCH_3)_2]ClO_4$ (M = Ni, Cu)[a]

	M = Ni	M = Cu
Bond Distances, Å		
Cl_4-O_1	1.432 (11)	1.404 (22)
Cl_4-O_2	1.415 (8)	1.412 (14)
Cl_4-O_3	1.392 (10)	1.424 (16)
Cl_4-O_4	1.412 (12)	1.399 (23)
Bond Angles, Deg		
$O_1-Cl_4-O_2$	112.8 (7)	110.6 (12)
$O_1-Cl_4-O_3$	107.9 (7)	111.7 (12)
$O_1-Cl_4-O_4$	108.6 (8)	107.3 (14)
$O_2-Cl_4-O_3$	105.5 (6)	103.1 (11)
$O_2-Cl_4-O_4$	111.7 (6)	111.8 (12)
$O_3-Cl_4-O_4$	110.2 (8)	112.4 (15)

[a] Standard deviations in parentheses.

minimization of steric interactions between hydrogen atoms on each $-NCH_2CH_2N-$ chain within the ligand. By contrast, in the complex $NiCl_3L^+C_3\cdot H_2O$, the Dabconium ligand is bisected by a crystallographic mirror plane such that one ring is planar and presumably the other (related) rings closely approach planarity. The average N–C and C–C distances of 1.493 (9), 1.525 (13) and 1.494 (7), 1.513 (7) Å for the nickel and copper complex ions, respectively, are in close agreement with the values obtained for the monoDabconium compound[18] and the $(HLCH_3)^{2+}$ cation.[6] As a final point we note that in the $[MCl_3(L^+CH_3)_2]^+$ complexes, when allowance is made for the nonplanarity of the $-CH_2CH_2-$ chains, the two ligands coordinate such that the approximate C_2 axis along the $M-Cl_1$ bond is retained and this feature is evident in Figure 1.

The dimensions of the perchlorate ions in the two complexes are listed in Table XI. The oxygen atoms exhibit the extensive anisotropic thermal motion typical of uncoordinated perchlorate and the root-mean-square amplitudes listed in Table VIII give an indication of the anisotropy. The average Cl–O distance of 1.411 (9) Å (eight values) is in the region commonly reported for this dimension. There is no evidence of any static disorder and the bond angles are closer to the anticipated tetrahedral values than is often found.

A view of the contents of one unit cell, excluding the perchlorate ions, is illustrated in Figure 2. In projection the molecular z axes (taken normal to the MCl_3 planes) of complexes I and III are almost orthogonal to those of complexes II and IV. Since these axes are aligned almost along the body diagonals of the pseudocubic unit cell, the other two projections appear to be very similar to the (010) projection, with orthogonal pairs of complex ions. The four independent

mutual angles of inclination of the molecular z axes are 109.5, 109.9, 113.1, and 105.4°. As noted in the Introduction the orientations of the complexes effectively preclude obtaining reliable single-crystal measurements of magnetic anisotropies and molecular polarizations. The complex ions pack in an approximate face-centered cubic manner with the perchlorate ions occupying the octahedral holes, so that the overall structural arrangement is of the NaCl type.

Supplementary Material Available: Listings of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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