debted to Mr. P. Simms for the design of the neutron cryostat.

**Supplementary Material Available:** A listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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# Spectroscopic and Structural Investigation on the Pentachloro- and (Mixed-pentahalo)cuprates(II) of the *N*-(2-Ammoniumethyl)piperazinium Cation. The First Case of Monomeric Pentahalocuprate(II) Having Square-Pyramidal Structure. Crystal and Molecular Structure of the (*N*-(2-Ammoniumethyl)piperazinium) Pentachlorocuprate(II) Dihydrate

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*Contribution from the Consiglio Nazionale delle Ricerche, Rome, Italy, Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy, and Istituto di Chimica, Facolta di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy.*
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**Abstract:** Some compounds of the type (N(2amet)pipzH$_3$)CuCl$_m$Br$_{5-m}$·$n$H$_2$O (N(2amet)pipzH$_3$ = *N*-(2-ammoniumethyl)-piperazinium cation; $m = 5$ and $n = 2$; $m = 4, 3, 2, 1$ and $n = 1$) were prepared and investigated by means of X-ray powder, electronic and vibrational spectra, and magnetic moments. For one of them, (N(2-amet)pipzH$_3$)CuCl$_5$·2H$_2$O, the crystal structure was also determined by three-dimensional X-ray diffraction. The substance crystallizes in space group $P2_1/a$ with lattice constants $a = 17.991$ (6) Å, $b = 9.249$ (3) Å, $c = 9.560$ (4) Å, $\beta = 98.14$ (5)°, and $Z = 4$. The intensity data were collected with a Philips PW 1100 automatic four-circle diffractometer using Mo K$\alpha$ radiation. The structure was solved by three-dimensional Patterson and Fourier methods and parameters were refined by least-squares calculations to a conventional $R$ factor of 3.4% for 1652 independent reflections [$I > 3\sigma(I)$]. The structure consists of discrete CuCl$_5$$^{3-}$ and [N(amet)pipzH$_3$]$^{3+}$ ions and of two water molecules of crystallization. The CuCl$_5$$^{3-}$ anion has a slightly distorted square-pyramidal coordination. A very complex network of hydrogen bonds was observed and considered to be responsible for this new geometry for CuL$_5$ (L = unidentate ligand) complexes. The magnetic and spectroscopic results for all the compounds indicate that they are isomorphous. The far-IR and Raman spectra of the square-pyramidal CuCl$_5$$^{3-}$ ion were also discussed and assigned. The presence of strong hydrogen bonds was also observed in the infrared spectra.

## Introduction

The copper(II) halides are rather interesting, showing a great variety of coordination numbers and geometries,[2] and, as they contain unidentate ligands, are also probably of the greatest potential interest from an electronic structural viewpoint.

In the case of pentacoordinated complexes, although differences in energy between trigonal bipyramidal and square-pyramidal structures should be small, as a general tendency, we can expect the trigonal bipyramidal structure to be favored with respect to the square-pyramidal one, whenever the five ligands are equivalent or nearly so with no particular steric constraints.[3,4] In accordance with these considerations, the only known monomeric pentahalocuprate ions (CuX$_5$$^{3-}$ (X = Cl, Br) and CuCl$_2$Br$_3$$^{3-}$) present trigonal bipyramidal structures,[5,6] and other pentacoordinated chlorocuprates(II), such as (CH$_3$)NH$_2$CuCl$_3$,[7] PhCH$_2$CH$_2$NMeH$_2$CuCl$_3$,[8]

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**Table I.** Colors, Conventional Chemical Analysis Results, and Decomposition Points

| compd | color | C, % calcd | C, % found | H, % calcd | H, % found | N, % calcd | N, % found | mp, °C dec |
|---|---|---|---|---|---|---|---|---|
| $[N(2amet)pipzH_3]CuCl_5\cdot2H_2O$[a] | yellow-green | 17.60 | 17.78 | 5.42 | 5.36 | 10.27 | 10.26 | 204 |
| $[N(2amet)pipzH_3]CuCl_4Br\cdot H_2O$ | orange-yellow | 16.53 | 16.58 | 4.63 | 4.94 | 9.65 | 9.37 | 208 |
| $[N(2amet)pipzH_3]CuCl_3Br_2\cdot H_2O$ | red-orange | 15.00 | 15.24 | 4.62 | 4.69 | 8.78 | 8.58 | 205 |
| $[N(2amet)pipzH_3]CuCl_2Br_3\cdot H_2O$ | red-brown | 13.73 | 14.10 | 3.84 | 3.67 | 8.01 | 8.06 | 197 |
| $[N(2amet)pipzH_3]CuClBr_4\cdot H_2O$ | brown | 12.66 | 12.76 | 3.54 | 3.51 | 7.39 | 7.23 | 187 |

[a] Cl % = 43.32 (43.34), found (calcd).

**Table II.** Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

| atom | *x* | *y* | *z* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 0.326 35(4) | 0.584 36(8) | 0.789 40(7) | 3.27(3) | 2.43(3) | 2.12(2) | −0.27(3) | 0.51(2) | −0.01(3) |
| Cl(1) | 0.3751(1) | 0.7721(2) | 0.6755(2) | 4.63(8) | 3.08(7) | 2.93(6) | −0.73(6) | 0.50(6) | 0.39(5) |
| Cl(2) | 0.4147(1) | 0.6333(2) | 0.9853(1) | 4.24(7) | 4.30(8) | 2.30(6) | −1.45(6) | 0.12(5) | 0.18(5) |
| Cl(3) | 0.2630(1) | 0.4420(2) | 0.9369(1) | 4.22(7) | 4.47(8) | 2.37(5) | −1.39(6) | 0.70(5) | 0.11(6) |
| Cl(4) | 0.2217(1) | 0.5811(2) | 0.6211(1) | 3.23(6) | 2.87(6) | 2.68(6) | 0.04(6) | 0.46(5) | 0.01(5) |
| Cl(5) | 0.3902(1) | 0.3694(2) | 0.6845(2) | 3.45(7) | 2.91(6) | 3.69(7) | 0.17(5) | 0.77(5) | −0.35(5) |
| N(1) | 0.2849(3) | 0.7243(5) | 0.3541(5) | 3.30(24) | 2.24(22) | 2.68(22) | 0.43(18) | 0.36(18) | −0.11(19) |
| C(2) | 0.3607(4) | 0.7532(7) | 0.3208(7) | 3.59(29) | 2.90(28) | 3.00(27) | 0.35(24) | 0.71(23) | −0.05(23) |
| C(3) | 0.4095(3) | 0.6203(7) | 0.3478(7) | 2.83(27) | 2.98(29) | 3.29(27) | 0.05(22) | 0.26(21) | −0.64(22) |
| N(4) | 0.3741(3) | 0.4934(5) | 0.2626(5) | 3.09(22) | 2.66(22) | 1.76(19) | 0.39(17) | 0.64(17) | 0.37(16) |
| C(5) | 0.2983(3) | 0.4654(6) | 0.3013(6) | 2.75(26) | 2.43(27) | 2.81(26) | −0.09(21) | 0.90(21) | −0.23(21) |
| C(6) | 0.2491(3) | 0.5977(6) | 0.2743(6) | 3.10(27) | 2.51(27) | 2.99(26) | 0.41(22) | −0.01(21) | −0.07(22) |
| C(7) | 0.4274(4) | 0.3662(7) | 0.2837(7) | 4.25(32) | 3.11(29) | 2.99(27) | 1.81(25) | 0.43(24) | 0.31(23) |
| C(8) | 0.4055(4) | 0.2400(7) | 0.1847(7) | 4.99(36) | 2.70(29) | 4.05(31) | 0.32(27) | 2.13(28) | 0.19(25) |
| N(9) | 0.4180(4) | 0.2695(6) | 0.0367(6) | 5.42(32) | 3.06(26) | 3.31(26) | −0.82(24) | 1.62(23) | −0.62(21) |
| O(1) | 0.5250(4) | 0.9234(8) | 0.3805(11) | 8.05(43) | 6.05(37) | 22 24(87) | −1.32(34) | 5.13(51) | −2.07(51) |
| O(2) | 0.4235(5) | 1.0015(7) | 0.9210(9) | 17.52(77) | 4.88(34) | 14.20(62) | 3.50(41) | −8.10(56) | −4.95(39) |

| atom | *x* | *y* | *z* | *B*, Å² | atom | *x* | *y* | *z* | *b*, Å² |
|---|---|---|---|---|---|---|---|---|---|
| H(11) | 0.257(4) | 0.794(9) | 0.335(8) | 3.59[b] | H(61) | 0.196(4) | 0.579(8) | 0.303(7) | 3.58 |
| H(12) | 0.282(4) | 0.708(9) | 0.452(8) | 3.59 | H(62) | 0.234(4) | 0.618(8) | 0.158(8) | 3.58 |
| H(21) | 0.384(4) | 0.827(9) | 0.386(8) | 4.10 | H(71) | 0.483(4) | 0.416(9) | 0.273(8) | 4.18 |
| H(22) | 0.354(4) | 0.784(9) | 0.219(8) | 4.10 | H(72) | 0.431(4) | 0.334(9) | 0.386(8) | 4.18 |
| H(31) | 0.465(4) | 0.631(8) | 0.330(8) | 4.00 | H(81) | 0.353(5) | 0.195(9) | 0.176(8) | 4.40 |
| H(32) | 0.413(4) | 0.585(9) | 0.456(8) | 4.00 | H(82) | 0.442(4) | 0.157(9) | 0.211(8) | 4.40 |
| H(41) | 0.372(4) | 0.521(8) | 0.181(8) | 3.18 | H(91) | 0.376(5) | 0.333(10) | 0.002(9) | 4.85 |
| H(51) | 0.277(4) | 0.394(8) | 0.247(8) | 3.61 | H(92) | 0.473(5) | 0.322(9) | 0.033(8) | 4.85 |
| H(52) | 0.304(4) | 0.439(9) | 0.401(8) | 3.61 | H(93) | 0.424(5) | 0.184(10) | −0.005(9) | 4.85 |

[a] The form of anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] The fixed isotropic temperature factor assigned to hydrogen atoms is 1.0 Å² greater than the last isotropic temperature factor of the bonded atom.

$pqCu_2Cl_6$,[9] $(Co(en)_3)_2(Cu_2Cl_8)Cl_2\cdot2H_2O$,[10] and bis(4-benzylpiperidinium)hexachlorodicuprate(II),[11] show intermediate structure between trigonal bipyramidal and square pyramidal. The monomeric $CuCl_5^{3-}$ unit with regular square-pyramidal structure has not until now been isolated.

In this paper we report a series of pentahalocuprates(II) of *N*-(2-ammoniumethyl)piperazinium trication (hereafter abbreviated as $N(2amet)pipzH_3$) having square-pyramidal or distorted square-pyramidal structures, in order to rationalize the conditions and the forces which have a determining influence on this configuration.

This paper also represents an extension of our previous investigations on the effects of cation dimension, hydrogen bonding, and inter- and intramolecular contacts on the geometry of the halocuprates(II).[11-14]

## Experimental Section

**Preparation of the *N*-(2-Ammoniumethyl)piperazinium Salts.** The *N*-(2-ammoniumethyl)piperazinium salts precipitate when a methanolic amine solution is neutralized with concentrated or gaseous hydrogen halides. The compounds may be recrystallized by dissolving them in the minimum amount of water, adding methanol, and allowing them to stand at 0 °C for some hours.

**Preparation of the Complexes.** $(N(2amet)pipzH_3)CuCl_5\cdot2H_2O$ complex was prepared by adding concentrated hydrogen chloride to

**Table III.** Interatomic Distances and Esd's (Å) for $[N(2amet)pipzH_3]CuCl_5\cdot2H_2O$

| | | | |
|---|---|---|---|
| A. Within $CuCl_5^{3-}$ Anion | | | |
| Cu-Cl(1) | 2.289(2) | Cl(1)···Cl(5) | 3.734(2) |
| Cu-Cl(2) | 2.323(2) | Cl(2)···Cl(3) | 3.230(2) |
| Cu-Cl(3) | 2.340(2) | Cl(2)···Cl(5) | 3.750(2) |
| Cu-Cl(4) | 2.297(2) | Cl(3)···Cl(4) | 3.269(2) |
| Cu-Cl(5) | 2.570(2) | Cl(3)···Cl(5) | 3.615(2) |
| Cl(1)···Cl(2) | 3.214(2) | Cl(4)···Cl(5) | 3.588(2) |
| Cl(1)···Cl(4) | 3.257(2) | | |
| B. Within $[N(2amet)pipzH_3]^{3+}$ Cation | | | |
| N(1)-C(2) | 1.469(8) | C(3)-H(32) | 1.08(9) |
| N(1)-C(6) | 1.493(7) | N(4)-H(41) | 0.82(8) |
| C(2)-C(3) | 1.511(9) | C(5)-H(51) | 0.89(7) |
| C(3)-N(4) | 1.516(7) | C(5)-H(52) | 0.98(9) |
| N(4)-C(5) | 1.486(8) | C(6)-H(61) | 1.05(7) |
| N(4)-C(7) | 1.513(9) | C(6)-H(62) | 1.12(8) |
| C(5)-C(6) | 1.510(9) | C(7)-H(71) | 1.12(8) |
| C(7)-C(8) | 1.518(9) | C(7)-H(72) | 1.01(9) |
| C(8)-N(9) | 1.490(9) | C(8)-H(81) | 1.02(8) |
| N(1)-H(11) | 0.82(9) | C(8)-H(82) | 1.02(9) |
| N(1)-H(12) | 0.96(8) | N(9)-H(91) | 0.97(10) |
| C(2)-H(21) | 0.98(7) | N(9)-H(92) | 1.10(9) |
| C(2)-H(22) | 1.01(9) | N(9)-H(93) | 0.90(8) |
| C(3)-H(31) | 1.04(8) | | |

**Table IV.** Bond Angles and Esd's (deg) for $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$

| | | | |
|---|---|---|---|
| A. Within $CuCl_5^{3-}$ Anion | | | |
| Cl(1)-Cu-Cl(2) | 88.33(3) | Cl(2)-Cu-Cl(4) | 165.1(1) |
| Cl(1)-Cu-Cl(3) | 164.9(2) | Cl(2)-Cu-Cl(5) | 99.95(3) |
| Cl(1)-Cu-Cl(4) | 90.48(3) | Cl(3)-Cu-Cl(4) | 89.65(3) |
| Cl(1)-Cu-Cl(5) | 100.26(3) | Cl(3)-Cu-Cl(5) | 94.73(3) |
| Cl(2)-Cu-Cl(3) | 87.71(3) | Cl(4)-Cu-Cl(5) | 94.82(2) |
| B. Within $[N(2amet)pipzH_3]^{3+}$ Cation | | | |
| N(1)-C(2)-C(3) | 110.5(2) | C(3)-N(4)-C(7) | 108.7(2) |
| N(1)-C(6)-C(5) | 110.3(2) | N(4)-C(5)-C(6) | 110.7(2) |
| C(2)-C(3)-N(4) | 110.4(2) | N(4)-C(7)-C(8) | 114.2(3) |
| C(2)-N(1)-C(6) | 112.3(2) | C(5)-N(4)-C(7) | 114.7(3) |
| C(3)-N(4)-C(5) | 109.4(2) | C(7)-C(8)-N(9) | 113.0(2) |

a blue solution containing the amine and $CuCl_2 \cdot 2H_2O$, in a 2:1 stoichiometric ratio, until the solution became dark green. Further addition of hydrogen chloride, methanol, or ethanol separated a well-crystallized compound.

$(N(2amet)pipzH_3)CuCl_mBr_{5-m} \cdot H_2O$ ($m$ = 4, 3, 2, 1) complexes precipitated by adding methanol to a solution containing the hydrohalide and the metal salts, in the appropriate stoichiometric ratio, dissolved in the minimum amount of water.

Some attempts to prepare the corresponding pentabromocuprate(II) were not successful.

**Physical Measurements.** The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra, as Nujol or hexachlorobutadiene mulls on KBr pellets as support (4000-250 $cm^{-1}$) and Nujol mulls on polythene as supports (500-60 $cm^{-1}$), were recorded with a Perkin-Elmer 180 spectrophotometer. Raman spectra were recorded on a Ramanor HG-2S Jobin-Yvon instrument by use of a 5145-Å argon-ion laser line on solid samples on a rotative cell. The room temperature magnetic moments were measured with the Gouy method by using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants.

**Crystallographic Data Collection.** The crystal selected for X-ray data collection had approximate dimensions 0.38 × 0.20 × 0.11 mm, and was mounted along its longest dimension on a glass fiber. Data were collected at room temperature on a Philips PW1100 automatic four-circle diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). Refined cell dimensions and their estimated standard deviations were obtained from 24 accurately centered reflections using the standard control program of the PW1100[15] system with a randomly oriented crystal. Crystals are monoclinic: $a$ = 17.991 (6) Å, $b$ = 9.249 (3) Å, $c$ = 9.560 (4) Å, $\beta$ = 98.14 (5)°, and $V$ = 1574.7 Å$^3$, which for $Z$ = 4 gives $d_{calcd}$ = 1.725 g cm$^{-3}$ ($d_{obsd}$ = 1.72 g cm$^{-3}$, by flotation in $CCl_4$-$CBr_4$ solution). Integrated intensities for $-h_{max} \leq h \leq h_{max}$ with $k$ and $l \geq 0$ reflections and $3° < \theta < 24°$ were measured by using the $\theta$-$2\theta$ scan method, a scan speed of 2.4° min$^{-1}$, and a scan width of 1.1°. Stationary background counts were taken for 10 s at each end of the scan. The intensities of two standard reflections monitored at 120-reflection intervals showed no significant variations. An examination of the complete data set revealed systematic absence $0k0$ for $k = 2n + 1$ and $h0l$ for $h = 2n + 1$; the space group $P2_1/a$ ($C_{2h}^5$, no. 14) is thereby determined uniquely. A total of 2467 independent reflections were measured, and the recorded intensities and $\sigma(I)$ values evaluated as (peak counts + total background counts)$^{1/2}$ and corrected for Lorentz and polarization factors, but not for absorption: 1652 reflections for which $I > 3\sigma(I)$ were denoted observed and were used in the structure analysis.

**Solution and Refinement of the Structure.** The scattering factors for $Cu^{2+}$, $Cl^-$, N, C, O, and H from published tables[16] were used with real and imaginary anomalous dispersion corrections applied for $Cu^{2+}$ and $Cl^-$. The function minimized during least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$; discrepancy indices used below are defined as $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w$ is the weighting factor. Data were placed on an approximate absolute scale by means of a Wilson plot. The position of the Cu atom was determined from a three-dimensional Patterson map;[17] a difference-Fourier synthesis revealed the locations of the Cl atoms and an observed-Fourier synthesis, phased by contribution of the Cu and the Cl atoms, the positions of all nonhydrogen atoms. Block-diagonal least-squares refinement of atomic positional and isotropic thermal parameters, using unit weights, converged to a $R$ of 0.089 and $R_w$ of 0.093. All hydrogen atoms were located in a subsequent difference-Fourier map, except those on water oxygen atoms; attempts to locate these four hydrogen atoms were unsuccessful even after the final least-squares refinement, probably owing to the very large thermal motion parameters of the atoms to which they are bonded. The isotropic thermal parameters of the hydrogen atoms were set 1.0 Å$^2$ greater than the bonded atom. Some further cycles of full-matrix least-squares refinement, employing anisotropic thermal parameters for the nonhydrogen atoms, and holding fixed the thermal parameters of the hydrogen atoms, led to convergence and a final $R$ value of 0.034 and a $R_w$ of 0.037. In the final least-squares cycle the shifts in all parameters were less than 0.2 an esd, except those of three N(9)-bonded hydrogen atoms, for which this value was about 0.5. The "goodness of fit," defined as $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $N_o$ = 1649 is the number of reflections and $N_v$ = 208 the numbers of parameters varied, was 1.67. Unit weights were used also in the final cycles of refinements because the quantity $w(|F_o| - |F_c|)^2$ showed no serious dependence on $|F_o|$ or on $(\sin \theta)/\lambda$, and the resulting weighting scheme was better than that obtained with $w = 1/\sigma^2(F)$, previously tested. During the refinement zero weight was assigned to three strong low-order reflections with $F_o$ systematically less than $F_c$, which may be affected by secondary extinction. A final difference-Fourier map showed the largest peaks, which had heights around 0.35 e Å$^3$, near the oxygen atoms. The positional and thermal parameters along with their standard deviations are given in Table II.

**Analyses.** Nitrogen, carbon, and hydrogen were analyzed using a

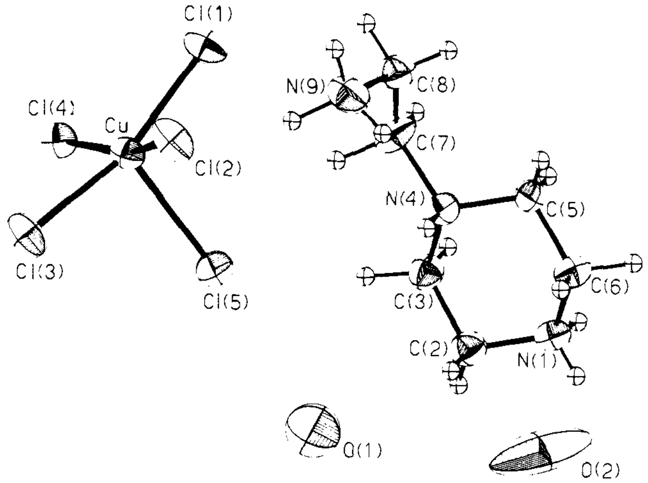

**Figure 1.** ORTEP drawing of the $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$ molecule showing the labeling scheme and thermal motion ellipsoids (50%) for nonhydrogen atoms. Hydrogen atoms are represented as spheres of radius 0.1 Å.

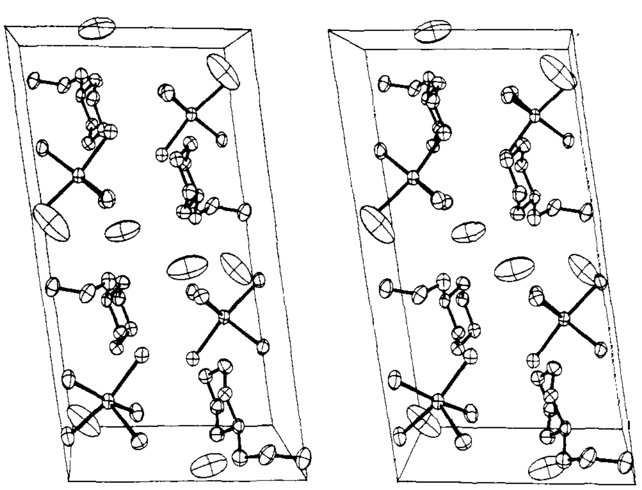

**Figure 2.** Stereoview of the cell of $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$ down the $b$ axis with the $a$ axis vertical and the $c$ axis horizontal. The ellipsoids enclose 50% probability of thermal motion; the hydrogen atoms have been omitted for clarity.

**Table V.** Ideal and Observed Angles (deg) for Pentacoordinate Chlorocuprates(II)

| complex | shape determining $\delta'$ angles ($e_3$, $e_1$, and $e_2$) | $\delta$ angles ($a_2$ and $a_5$ and remaining angles) |
|---|---|---|
| ideal trigonal bipyramid[a] | 53.1<br>53.1, 53.1 | 101.5, 101.5, 101.5,<br>101.5, 101.5, 101.5 |
| $[Cr(NH_3)_6][CuCl_5]$[b] | 55.0<br>55.0, 55.0 | 100.4, 100.4, 100.4,<br>100.4, 100.4, 100.4 |
| $(nmpH)CuCl_3$[c] | 45.0<br>52.9, 65.1 | 92.8, 97.9, 96.3, 100.5,<br>108.8, 109.4 |
| $[Co(en)_3]_2$ $[Cu_2Cl_8]Cl_3\cdot 2H_2O$[d] | 39.9<br>54.7, 69,2 | 91.9, 92.5, 99.1, 99.1,<br>110.8, 112.0 |
| $[Paraquat]Cu_2Cl_6$[e] | 31.7<br>61.8, 68.8 | 85.7, 88.0, 105.4, 107.4,<br>107.5, 110.6 |
| $(4BzpipdH)_2Cu_2Cl_6$[f] | 29.5<br>54.7, 58.2 | 85.1, 89.7, 104.8, 108.4,<br>110.1, 110.6 |
| $(CH_3)_2NH_2CuCl_3$[g] | 20.2<br>67.5, 70.3 | 82.5, 87.9, 107.4, 111.4,<br>112.5, 114.5 |
| $[N(2amet)pipzH_3]$ $CuCl_5\cdot 2H_2O$[h] | 0.1<br>74.0, 77.9 | 74.9, 77.2, 116.9, 119.1,<br>120.0, 122.1 |
| ideal tetragonal pyramid[a] | 0.0<br>75.7, 75.7 | 75.7, 75.7, 119.8, 119.8,<br>119.8, 119.8 |

[a] The Cu–Cl$_a$ to Cu–Cl$_e$ bond length ratio for idealized models is set at unity and a Cl$_a$–Cu–Cl$_e$ (basal) angle of 102° (mean value of observed ranges) is assumed for $C_{4v}$ model. [b] Reference 5. [c] Reference 8. [d] Reference 10. [e] Reference 9. [f] Reference 11. [g] Reference 7. [h] This work.

C. Erba elemental analyzer. The chlorine was directly determined in an aqueous solution of the $[N(2amet)pipzH_3]CuCl_5Å2H_2O$ complex with the Volhard method.

## Results and Discussion

The analytical results are reported in Table I. The compounds, which are crystalline and stable in air, present empirical formulas of the type$[N(2amet)pipzH_3]CuCl_mBr_{5-m}\cdot nH_2O$ ($m = 5$ and $n = 2$; $m = 4, 3, 2, 1$ and $n = 1$). All the mixed-halocuprates(II) are true compounds and not mixtures of $CuX_5^{3-}$ species as is suggested by the charge-transfer bands of their electronic spectra, which are characteristic of the ligands bonded to the $Cu^{2+}$ ions, from their powder spectra, and from the reproducible analyses and decomposition points, measured on several crystallizations.

**Description of the Structure.** A drawing of the structure, showing the labeling scheme, is given in Figure 1 and a drawing of the unit cell contents in Figure 2. The positional and thermal parameters, the bond lengths, and the bond angles are listed in Tables II, III, and IV, respectively.

The salt consists of discrete $CuCl_5^{3-}$ and $[N(2amet)pipzH_3]^{3+}$ ions and of two water molecules of crystallization; the cation is linked to the $CuCl_5^{3-}$ anion and to a water molecule by hydrogen bonds, which may be also supposed to be between the anion and a water molecule and between the water molecules.

Bond distances and angles of the $CuCl_5^{3-}$ anion indicate a slightly distorted square-pyramidal coordination. The mean Cu–Cl bond distance of the four equatorial chlorine atoms is 2.318 Å with a maximum deviation of 0.043 Å and the ratio of axial (2.570 Å) to mean equatorial bond lengths is 1.11; the bond angles between adjacent equatorial Cl atoms average to 89.04° with a maximum deviation of 2.77°, while the mean value of the four axial Cl–Cu–Cl bond angles is 97.44° with a maximum deviation of 5.53°. The Cu atom is displaced 0.299 Å in direction of the axial Cl(5) atom from the least-squares plane of the equatorial Cl atoms, whose equation, referred to the crystallographic axes, is $-0.5572x + 0.7392y + 0.4534z = 4.444$ and from which none of the chlorine atoms deviate more than ±0.0012 Å.

**Table VI.** Hydrogen Bonding Distances and Angles with Their Esd's.

| atom 1 atom 2 atom 3 | 2–3, Å | 1–3, Å | ∠1–2–3, deg |
|---|---|---|---|
| N(1)–H(12)···Cl(1) | 2.58(9) | 3.295(6) | 131(4) |
| O(2)–not found···Cl(1) | | 3.192(8) | |
| N(4)[a]–H(41)[a]···Cl(2) | 2.36(8) | 3.128(5) | 157(4) |
| N(9)[b]–H(92)[b]···Cl(2) | 2.10(8) | 3.176(7) | 165(3) |
| N(9)[a]–H(91)[a]···Cl(3) | 2.28(9) | 3.237(7) | 167(5) |
| N(1)–H(12)···Cl(4) | 2.38(8) | 3.223(6) | 146(3) |
| O(1)[b]–not found···Cl(5) | | 3.212(7) | |
| N(9)–H(93)···O(2)[c] | 1.82(8) | 2.722(8) | 172(2) |
| O(1) not found O(1)[d] | | 2.94(1) | |
| O(2) not found O(2)[e] | | 2.95(1) | |

Superscripts refer to the following transformations of the coordinates: [a] $x, y, z + 1$. [b] $1 - x, 1 - y, 1 - z$. [c] $x, 1 - y, 1 - z$. [d] $1 - x, 2 - y, 1 - z$. [e] $1 - x, 2 - y, 2 - z$. [f] $x, 1 - y, z$.

A more precise description of the geometry was obtained by means of the Muetterties and Guggenberger criterion,[18] evaluating the dihedral angles formed by the normals to adjacent triangular faces of the coordination polyhedron; a subset of these angles ($e_n$) can be chosen as defining the shape and correlating between limiting forms. The results, reported in Table V, along with the dihedral angles for the two idealized geometries $D_{3h}$ and $C_{4v}$ and with the calculated values for several pentacoordinate chlorocuprates(II),[5,7-11] indicate for our complex a strictly square-pyramidal geometry, very close to that of $Ni(CN)_5^{3-}$,[19] reported as one of the best examples of $ML_5$ complexes having $C_{4v}$ symmetry.[18]

The piperazine ring of the cation shows the usual "chair" conformation with torsion angles ranging, as absolute value, from 55.8 to 58.5°, and with the N(1) and the N(4) atoms displaced 0.640 and −0.693 Å, respectively, from the least-squares plane defined by the four C atoms, ±0.0004 Å being the deviations of the C atoms from their plane.

The ethylammonium group is bonded to the piperazine ring in the equatorial position.

The C–N bond lengths of the cation average 1.495 Å, while the mean value of C–C bond lengths is 1.513 Å. Either the C–N bond lengthening or the C–C bond shortening, with respect to their expected values, are in good agreement with the results found for the piperazine ring of *N*-phenylpiperazinium tetrachlorocuprate(II),[14] in which these values average to 1.502 and 1.505 Å, respectively.

A very complex network of ascertained and supposed hydrogen bonds was found; these involving hydrogen atoms of water molecules, for which no clear evidence was obtained, were judged probable only on the basis of the interatomic distances. The resulting ten hydrogen bonds are reported in Table VI, and a drawing is shown in Figure 3. Each $CuCl_5^{3-}$ anion, whose Cl atoms are all involved in hydrogen bonding, is linked to three cations and to two independent water molecules, while each cation bridges three anions and one O atom through five of the six N-bonded H atoms. Hydrogen bonding is completed by interactions between symmetry-related water molecules; an O(1)–O(2)′ distance of 3.22 (1) Å was considered out of range of hydrogen bonding. As a result, infinite two-dimensional hydrogen-bonded networks are formed in the *yz* plane of the crystal, which contains no other close intermolecular contacts.

The extensive and strong hydrogen bondings, on which the crystal packing depends, may have a more important role in stabilizing the square-pyramidal geometry, as, on diminishing the charge density at the ligand atoms, they minimize ligand-ligand electron repulsion; in trigonal-bipyramidal $CuCl_5^{3-}$ ion only weak hydrogen bonds are present.[5]

**Powder and Electronic Spectra, Magnetic Moments, and Far-Infrared and Raman Spectra.** The room temperature powder X-ray and electronic (Table VII and Figure 4) spectra

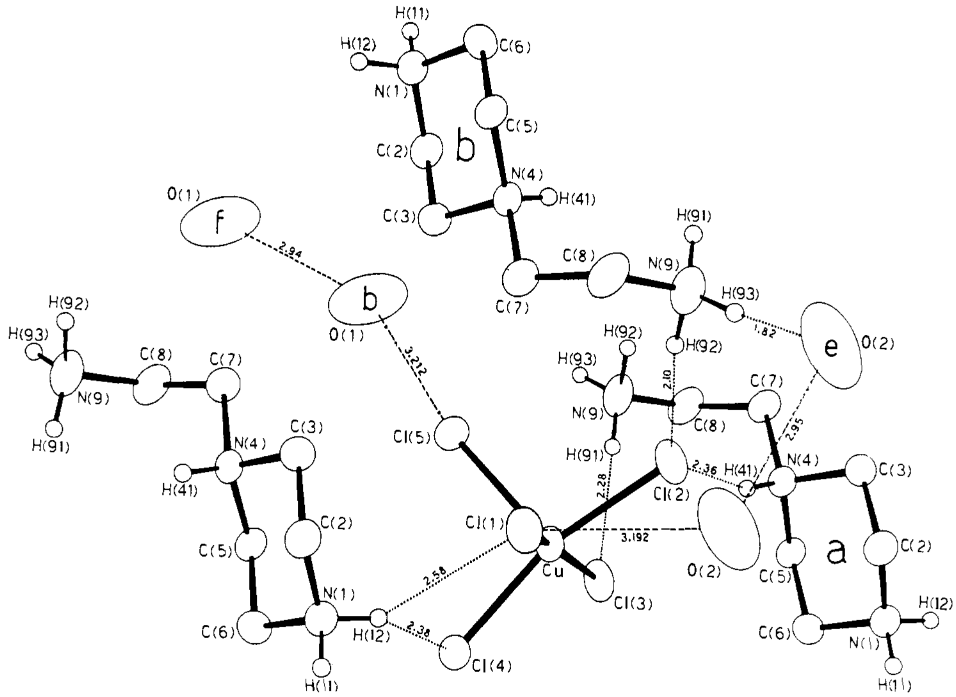

Figure 3. Ascertained (dotted lines) and supposed (dashed lines) hydrogen bonds in $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$. The projection is approximately along the *b* axis; C-bonded hydrogen atoms have been omitted for clarity. Small letters on atoms or on atom rings refer to the symmetry transformations of Table VI.

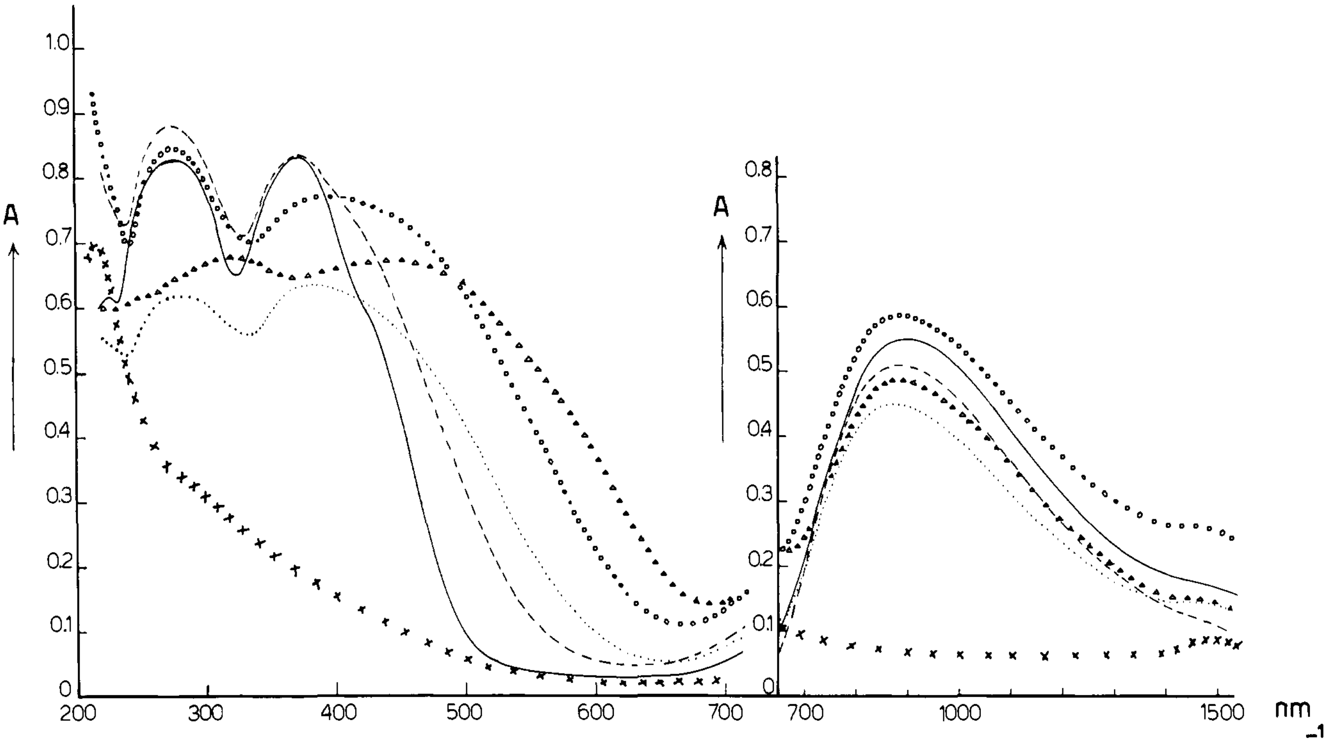

Figure 4. Solid-state electronic spectra of $[N(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$ (—), $[N(2amet)pipzH_3]CuCl_4Br{\cdot}H_2O$ (---), $[N(2amet)pipzH_3]CuCl_3Br_2{\cdot}H_2O$ (·····), $[N(2amet)pipzH_3]CuCl_2Br_3{\cdot}H_2O$ (ooo), and $[N(2amet)pipzH_3]CuClBr_4{\cdot}H_2O$ (△△△) complexes and of $N(2amet)pipz(HCl)_3$ salt (xxx).

of all the complexes are very similar to one other suggesting that they are isomorphous. In particular the solid electronic absorption spectra show a broad, unresolved band with a maximum at 11 050-11 430 $cm^{-1}$ with a poorly resolved shoulder on the low-frequency side assignable to d-d transitions. By comparing the spectra of our square-pyramidal $CuCl_5^{3-}$ ion with that of the rigorous trigonal bipyramidal $CuCl_5^{3-}$ ion,[20] we observe not only a shift of the d-d bands at higher frequency for our complex, but also a significant change of the band envelope. In fact for the trigonal bipyramidal stereochemistry the band maximum appears at lower energy with a low-intensity maximum or shoulder on the high-frequency side, while in the square-pyramidal stereochemistry the band maximum is at higher energy with a shoulder on the low-frequency side. This behavior is parallel to those reported for the five-coordinate $CuN_5$ chromophore.[21]

**Table VII.** Magnetic Moments and Electronic ($cm^{-1}$) Spectra

| | $\mu_{eff}$ | d-d bands | CT bands | | | |
|---|---|---|---|---|---|---|
| $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$ | 1.83 | 11 050 | 23 260 sh | 27 030 | 37 740 | |
| $[N(2amet)pipzH_3]CuCl_4Br \cdot H_2O$ | 1.80 | 11 240 | 22 470 sh | 27 030 | 37 740 | |
| $[N(2amet)pipzH_3]CuCl_3Br_2 \cdot H_2O$ | 1.85 | 11 320 | 22 220 sh | 26 040 | 37 040 | |
| $[N(2amet)pipzH_3]CuCl_2Br_3 \cdot H_2O$ | 1.83 | 11 360 | 21 740 sh | 25 640 | 33 330 | 37 040 |
| $[N(2amet)pipzH_3]CuClBr_4 \cdot H_2O$ | 1.79 | 11 430 | 19 610 sh | 22 220 | 24 390 sh | 37 740 |

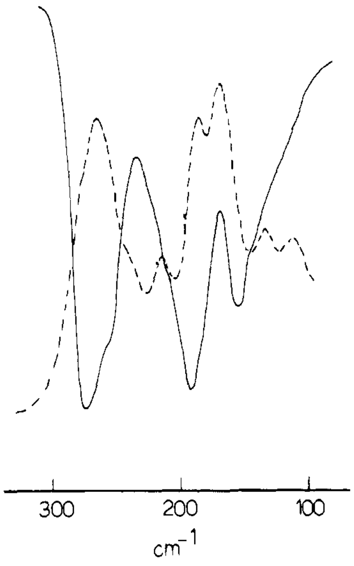

**Figure 5.** Far-IR (—) and Raman (---) spectra ($cm^{-1}$) of the solid $[N(2amet)pipzH_3]CuCl_5 \cdot 2H_2O$ complex.

The electronic spectra of the mixed complexes, although similar to that of the pentachlorocuprate, do not prove that they have the same square-pyramidal structure. A small change in atomic positions of halide atoms, due to the replacement of chlorine by bromine, would make the anion trigonal pyramidal or intermediate. Some distortion toward trigonal bipyramidal would probably go unnoticed in the spectra.

Room temperature magnetic moments of the compounds (Table VII), found to be 1.79-1.85 $\mu_B$, are within the range normally observed for copper(II) complexes.[22,23]

The far-IR and Raman spectra of the $CuCl_5^{3-}$ ion, reported in Table VIII and Figure 5, agree perfectly with a $C_{4v}$ symmetry, which results from its structural analysis. This type of symmetry allows four Raman-active and three infrared-active copper-chlorine stretching vibrations ($\Gamma_{\nu(CuCl)} = 2A_1(IR,R) + B_1(R) + E(IR,R)$). In particular, of the two $A_1$ bands, one originates from the copper-chlorine stretching mode, associated with the longest axial Cu-Cl bond (2.570 Å), and the other from the copper-chlorine symmetric stretching mode, associated with the shortest equatorial four $Cu-Cl_4$ bonds (2.289-2.340 Å), while the E band corresponds to the copper-chlorine asymmetric stretching mode, associated with the shortest equatorial $Cu-Cl_4$ bonds.[24,25] The asymmetric and symmetric stretching frequencies, associated with the shortest equatorial $Cu-Cl_4$ bonds, show a reversed intensity in the IR and Raman spectra.

The mixed halocuprates(II), for which Raman spectra may not be recorded as they decompose when irradiated with laser light, show far-IR spectra which cannot be unambiguously assigned, because of the uncertainty in their geometries and the possible presence of some isomers.[4] However, we tentatively suggest that the presence of Cu-Cl bonds in all the complexes may be associated with the strong band appearing around 270 $cm^{-1}$ and the presence of Cu-Br bonds with the very broad band around 200 $cm^{-1}$.

**Hydrogen Bonding.** The attempt to find evidence of the presence of intermolecular and intramolecular hydrogen bonding in the complexes by comparing their IR spectra with those of the hydrohalide salts and their deuterated analogues is not conclusive as the salts are also involved in strong hydrogen bonding. However, the positions of the N-H motions [3100-2400 (for undistinguished $\nu(^+NH_3)$, $\nu(^+NH_2)$, and $\nu(^+NH)$), 1580 ($\delta(^+NH_3)$), 1500 ($\delta(^+NH_2)$), and 1360 ($\delta(^+NH)$) $cm^{-1}$] are similar to those reported for other primary, secondary, and tertiary amine hydrohalides[12-14,26,27] involved in strong hydrogen bonds.

**Table VIII.** Vibrational Frequencies ($cm^{-1}$) of the $CuCl_5^{3-}$ Anion

| | E | $A_1$ | $B_1$ | $A_1$ |
|---|---|---|---|---|
| IR | 275 vs | 262 sh | | 190 vs |
| Raman | 278 sh | 265 vs | 214 m | 186 vs |

Another important feature of the IR spectra of all the complexes is the presence of the absorption characteristics of coordinated water molecules at around 3550 sh, 3450 s, and 1616 s $cm^{-1}$, which show the expected isotopic shifts on deuteration. As the antisymmetric and symmetric stretching frequencies appear well resolved when the water molecules exist as monomers, hydrogen bonded through only one of the hydrogen atoms,[28] the presence of unresolved bands in our complexes may be attributed to the complex hydrogen bonding, as described above, in which they are involved. Furthermore, as these bands appear in all the complexes, we may suggest that the presence of at least one water molecule should be of great importance in determining the stereochemistry of the anion.

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**Supplementary Material Available:** Bond angles involving hydrogen atoms and a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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# Lifetimes, Spectra, and Quenching of the Excited States of Polypyridine Complexes of Iron(II), Ruthenium(II), and Osmium(II)

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**Abstract:** The lifetimes of the excited states formed by 530-nm excitation of polypyridine complexes of iron(II) ($FeL_3^{2+}$) and osmium(II) ($OsL_3^{2+}$) have been determined by laser flash-photolysis techniques. The $FeL_3^{2+}$ lifetimes, measured in water at room temperature using picosecond absorption spectrometry, are as follows (L, $\tau \pm \sigma$ (ns)): 2,2′,2″-terpyridine (2.54 ± 0.13); 2,2′-bipyridine (0.81 ± 0.07); 4,4′-dimethyl(2,2′-bipyridine) (0.76 ± 0.04); 1,10-phenanthroline (0.80 ± 0.07); 4,7-(diphenyl sulfonate)-1,10-phenanthroline (0.43 ± 0.03). Lifetimes for the analogous complexes of osmium(II) lie in the range 10-100 ns under the same conditions. Unlike the excited states of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ ($\lambda_{max}$ 430-460 nm, $\epsilon \sim 5 \times 10^3\ M^{-1}\ cm^{-1}$), the excited state of $Fe(bpy)_3^{2+}$ does not luminesce or absorb significantly in the visible ($\epsilon < 10^3\ M^{-1}\ cm^{-1}$ at $\lambda \geq 350$ nm) but does exhibit intense absorption below ~325 nm. Rate constants for the quenching of the excited states of polypyridine complexes of osmium(II) and ruthenium(II) by ground-state polypyridine complexes of iron(II), ruthenium(II), and osmium(II) are reported and are ascribed to either electron-transfer or energy-transfer processes. The excited states of tris(2,2′-bipyridine)iron(II) and of bis(2,2′,2″-terpyridine)iron(II) undergo reaction with $Fe_{aq}^{3+}$ (0.5 M $H_2SO_4$, 25 °C) with a rate constant $\leq 1 \times 10^7\ M^{-1}\ s^{-1}$. Based on a comparison of its properties with those of the luminescent charge-transfer excited states of ruthenium(II) and osmium(II) polypyridine complexes the excited state of $FeL_3^{2+}$ is identified as a ligand-field state. The potential of the excited-state couple $Fe(bpy)_3^{3+} + e \rightleftharpoons {}^*Fe(bpy)_3^{2+}$ is estimated to be +0.1 V.

## Introduction

The photophysics and photochemistry of polypyridine complexes of ruthenium, especially tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$), have been extensively investigated in recent years.[2] Both kinds of study have implicated a major role for the luminescent metal-to-ligand charge-transfer excited state of complexes of this family. Similar conclusions have been drawn for the luminescent osmium(II) polypyridine complexes, although fewer data are available for this series.[3-7] By contrast, the analogous complexes of iron(II) have received relatively little attention. Fink and Ohnesorge[8] have found that $FeL_3^{2+}$ complexes (L = bpy, 1,10-phenanthroline = phen, 2,2′,2″-terpyridine = terpy, 2-methyl-1,10-phenanthroline) do not luminesce in absolute ethanol at either room temperature or 80 K. Kirk et al.,[9] using picosecond absorption spectrometry, determined a 0.83-ns lifetime for a nonemitting excited state of $Fe(bpy)_3^{2+}$, while Street et al.[10] have made analogous measurements on $Fe(phen)_3^{2+}$. Chum et al.[11] have obtained evidence for photoinduced oxidation of iron(II) chelates, including $Fe(bpy)_3^{2+}$, in aluminum chloride-ethylpyridinium bromide melts, while Phillips et al.[12] have reported that $Fe(bpy)_3^{2+}$ undergoes photooxidation in the presence of $Fe_{aq}^{3+}$.

In this work we have used laser flash-photolysis techniques to measure the lifetimes and spectra of the excited states of polypyridine complexes of ruthenium(II), osmium(II), and iron(II). In addition we have studied the quenching of the excited states of the osmium(II) and ruthenium(II) complexes by ground-state polypyridine complexes of iron(II), ruthenium(II), and osmium(II) and the quenching of $Fe(bpy)_3^{2+}$ and $Fe(terpy)_2^{2+}$ by $Fe_{aq}^{3+}$ ions. The mechanisms of these reactions and the properties of the excited states of the iron(II) complexes are discussed below.

## Experimental Section

**Materials.** The polypyridine ligands were used as received from the G. F. Smith Co. or from Fisher. The method of preparation of the osmium polypyridine complexes followed that given by Dwyer and co-workers.[13] The procedure for $Os(bpy)_3I_2$ is typical: 1.0 g of $K_2OsCl_6$ and 1.28 g of 2,2′-bipyridine were mixed with 50 mL of glycerol and heated at 240 °C for 1 h. The hot glycerol mixture was poured into 150 mL of hot water and then acidified with ~10 mL of 5 M HCl. The green solution was filtered, and solid potassium iodide was added to the filtrate. The resulting black powder was separated by filtration and washed with cold water and ether. The perchlorate salt was prepared from the iodide as follows. A 10% solution of sodium perchlorate was added dropwise to a solution of the iodide salt in hot water. The wall of the container was scratched with a glass rod and the solution was cooled in an ice bath. The solid perchlorate was collected on a filter, washed with ether, then dried in vacuo overnight. The purity of the products was ascertained by analysis for Os and halogen. When it proved difficult to separate $OsL_3^{2+}$ from unreacted ligand L (L, a phenanthroline derivative), the impure $OsL_3X_2$ was digested with benzene in order to dissolve the excess ligand.

Stock (0.01 M) solutions of the iron(II) polypyridine complexes were prepared by mixing 1.0 mmol of $Fe(NH_4)_2(SO_4)_2$, 3.1 mmol of

0002-7863/80/1502-1309$01.00/0