**O=Mo(TPP)OR (4).** Figure 4 shows the effect of addition of small amounts of ethyl alcohol upon the visible spectrum of a $CH_2Cl_2$ solution of the hydroxo complex **2**. Large excess results in a limiting spectrum identical with that of the ethoxo complex O=Mo(TPP)OEt (**4b**)[7] presented in Figure 1c. Therefore, equilibrium 3 exists is solution. However, in the presence of traces of base, it seems to be largely displaced toward the formation of the alkoxo complex. Visible spectra of several other alkoxo complexes are reported in Table I.

$$\mathrm{O{=}Mo(TPP)OH + ROH \rightleftharpoons O{=}Mo(TPP)OR + H_2O} \tag{3}$$

X-Band ESR spectra of O=Mo(TPP)X complexes in $CH_2Cl_2$ solution have been recorded at room temperature. As shown in Figure 5, they exhibit the typical feature previously reported.[1,8,919] The *g* values of the intense central set of nine lines are presented in Table II. We should point out that only small changes of this parameter are observed according to the nature of the axial X ligand.

## Conclusions

Several $[\mathrm{O{=}Mo(TPP)}]_n\mathrm{X}$ complexes ($n = 1$, X = Cl, OH, OMe, OEt, O(*i*-Pr), O(*t*-Bu); $n = 2$, X = O) have been characterized both in solution and in the solid state, by UV–visible, IR, and ESR spectroscopy. Extreme care must be taken for solution studies of these complexes as ligand exchanges occur extremely easily.[7,10] UV–visible spectra are very sensitive to the nature of the axial ligands whereas use of ESR spectroscopy seems to be inadequate for their identification.[20]

Our results clearly illustrate how unsecured are the structural assignments which rely only upon UV–visible data, as minor traces of impurities could dramatically change the nature of species present in the solution. On the other hand, extrapolation of structural results obtained in the solid state could easily be made safe by checking the IR or UV–visible spectra in both states.

Finally, our full characterization of O=Mo(TPP)OH puts an end to a ten year old discrepancy found in the literature about the existence of this complex.

**Acknowledgment.** We are indebted to J.-F. Dutel for the ESR measurements and to Dr. J.-C. Marchon for a generous gift of $^{18}$O-enriched water. This paper has benefited from discussions with Dr. I. Tkatchenko, whose comments and suggestions we gratefully acknowledge. We also thank the Centre National de la Recherche Scientifique for support of this work.

**Registry No. 1**, 68070-21-3; **2**, 28780-74-7; **3**, 61747-27-1; **4a**, 74751-79-4; **4b**, 65404-71-9; **4c**, 68046-15-1; **4d**, 68046-16-2.

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(19) Newton, C. M.; Davis, D. G. *J. Magn. Reson.* **1975**, *20*, 446.

(20) The same observation has been reported recently for O=Mo(TPP)X complexes (X = OEt, $O_2$, NCS, Cl, HCl, Br): Imamura, T.; Terui, M.; Takahashi, Y.; Namatatsu, T.; Fujimoto, M. *Chem. Lett.* **1980**, 89.

(21) Following the recommendation of a reviewer, the X-ray crystal structure determination of O=Mo(TPP)OMe has been undertaken. At the present level of refinement the complex clearly exhibits a trans oxo–methoxo axial ligation of the molybdenum atom, which is slightly displaced out of the mean plane of the porphyrin, toward the oxo ligand: Mentzen, B. F.; Ledon, H. J., manuscript in preparation.

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and Amoco Chemicals Corporation, Naperville, Illinois 60540

# Purine Complexes with Divalent 3d Metal Perchlorates[1a]

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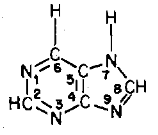
A series of $\mathrm{M(puH)_2(ClO_4)_2{\cdot}3H_2O}$ (M = Mn, Fe, Co, Ni, Cu, Zn) complexes with neutral purine (puH), presumably protonated at N(7), was prepared by interaction of ligand and metal salt in ethanol–triethyl orthoformate. The new complexes are hexacoordinated with two puH and three aqua ligands per metal ion and exclusively ionic perchlorate. Their magnetic moments are normal at room temperature, but magnetic data over the 300–80 K range are suggestive of magnetic exchange in bi- or polynuclear puH-bridged structures. Two possible structural types, involving both one unidentate terminal and one bidentate bridging puH ligand per metal ion, are discussed, viz., a linear oligomer with single-bridged >M<puH>M<puH– sequences and a double-bridged dimer of the $\mathrm{[(H_2O)_3(puH)M(PuH)_2M(puH)(OH_2)_3](ClO_4)_4}$ type. The former structural type seems more likely. Unidentate puH is assumed to coordinate through the N(9) nitrogen, while with bidentate bridging puH the bonding should be either through the N(1),N(9) or through the N(3),N(9) nitrogens.

## Introduction

Although metal complexes with biologically important substituted purines (i.e., adenine, guanine, hypoxanthine, xanthine, theophylline, 6-mercaptopurine, 8-azapurines, and their alkyl derivatives, nucleosides, and nucleotides) have been the subject of numerous studies,[2,3] there is a relative paucity of information regarding the corresponding complexes with unsubstituted purine (puH (I)). Only a few well-defined metal complexes with puH or the monodeprotonated anionic $pu^-$ species have been isolated and characterized. These include Na(pu),[4] Tl(pu),[5] $\mathrm{Hg(puH)X_2}$ (X = Cl, Br),[6] $\mathrm{[Cu(puH)Cl_2]{\cdot}HCl}$, $\mathrm{[Cu(puH)(OH_2)_2]SO_4{\cdot}3H_2O}$,[7] $\mathrm{[Cu(pu)_2}$-



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(1) (a) Speca, A. N.; Mikulski, C. M.; Iaconianni, F. J.; Pytlewski, L. L.; Karayannis, N. M. "Abstracts of Papers", the Joint American Chemical Society/Chemical Society of Japan Chemistry Congress, Honolulu, HI, April, 1979; American Chemical Society: Washington, DC, 1979; INOR 33. (b) USI Chemicals Co., Research Division, Cincinnati, OH 45237. (c) Department of Chemistry and Physics, Beaver College, Glenside, PA 19038. (d) Drexel University. (e) Amoco Chemicals Corp.

(2) Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211.

(3) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255.

(4) Lautiē, A.; Novak, A. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1971**, *273*, 908.

(5) Taylor, E. C.; Maki, Y.; McKillop, A. *J. Org. Chem.* **1969**, *34*, 1170.

(6) Lautiē, A.; Novak, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 1492.

(7) Weiss, R.; Venner, H. *Hoppe-Seyler's Z. Physiol. Chem.* **1963**, *333*, 169; **1965**, *340*, 138; **1966**, *345*, 122.

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**Table I.** Analyses and Some Properties of $M(puH)_2(ClO_4)_2{\cdot}3H_2O$ Complexes

| | | | anal.[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | % C | | % H | | % N | | % metal | | % Cl | |
| M | color | behavior on heating, °C[a] | calcd | found | calcd | found | calcd | found | calcd | found | calcd | found |
| Mn | cream white | 228, 253 | 21.91 | 22.27 | 2.57 | 2.62 | 20.44 | 20.87 | 10.02 | 9.78 | 12.94 | 13.15 |
| Fe | light yellow | 140, 195 | 21.88 | 21.54 | 2.57 | 2.40 | 20.41 | 20.33 | 10.17 | 10.56 | 12.91 | 13.36 |
| Co | orchid | 260, 270 | 21.75 | 22.19 | 2.56 | 2.72 | 20.30 | 20.14 | 10.68 | 10.29 | 12.84 | 13.11 |
| Ni | light blue | 285, 355 | 21.76 | 21.93 | 2.56 | 2.88 | 20.30 | 20.43 | 10.64 | 10.44 | 12.85 | 13.03 |
| Cu | sky blue | 235, 243 | 21.57 | 21.25 | 2.53 | 2.81 | 20.13 | 19.82 | 11.41 | 11.47 | 12.74 | 12.60 |
| Zn | cream white | 260, 280 | 21.50 | 21.38 | 2.53 | 2.77 | 20.06 | 20.35 | 11.70 | 12.08 | 12.69 | 12.37 |

[a] Temperatures of discoloration and decomposition, respectively (see text). [b] A number of water determinations, by Karl Fischer titration, gave the following results: found (calcd): M = Mn, 10.2 (9.86); M = Cu, 9.9 (9.71).

$(NH_3)(OH_2)]{\cdot}3H_2O$,[8] $W(CO)_5(puH)$, $[W(CO)_5(pu)]^-$, and $M(CO)(PPh_3)_2(pu)$ (M = Rh, Ir).[9] The precipitation of solid $Co^{2+}$ and $Ni^{2+}$ complexes with purine was also reported,[10] while several species of the types $[M(puH)(solvent)_n]^{2+}$ and/or $[M(pu)(solvent)_n]^+$ (M = Co, Ni, Zn) were identified by $^1H$ NMR studies of purine–metal salt mixtures in various solvents (water, water–acetone, dimethyl sulfoxide).[11-13] Formation constants for metal complexes of purine with 3d metal ions ($Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$) have been also determined.[13-15] For a number of purines the stabilities of their $Cu^{2+}$ complexes decrease along the series 6-(dimethylamino)purine > 2,6-diaminopurine > adenine > purine > hypoxanthine > 7-methylhypoxanthine > 9-methylhypoxanthine > xanthine > 1,3-dimethylxanthine.[15]

It was felt that synthetic and characterization studies of purine complexes with 3d metal salts (e.g., perchlorates, chlorides, nitrates) were in order. Accordingly, studies in this direction were undertaken, and the present paper deals with the complexes of divalent 3d metal (M = Mn, Fe, Co, Ni, Cu, Zn) perchlorates with puH.

## Experimental Section

**Preparative Method.** Reagent grade puH (Aldrich), hydrated metal perchlorates, and organic solvents were generally used. A 192-mg (1.6 mmol) sample of puH was dissolved in 15 mL of hot absolute ethanol, and the resulting solution was added to a stirred, hot (ca. 60 °C) solution of 0.4 mmol of the metal perchlorate in 20 mL of a 1:1 (v/v) mixture of ethanol and triethyl orthoformate (teof). With nickel(II), copper(II), and zinc(II) perchlorates, precipitates were obtained immediately, while with the rest of the metal(II) perchlorates studied (Mn, Fe, Co), solid complexes were precipitated upon cooling of the reaction mixture and addition of 100 mL of anhydrous diethyl ether. The new complexes were allowed to remain under the supernatant overnight, and then they were separated by filtration, washed with anhydrous diethyl ether on the filter, and stored in vacuo over anhydrous $CaSO_4$. The weights of the dry, solid new complexes ranged between 140 and 150 mg, corresponding to yields of 60–70% of the theoretical. All the preceding preparations and subsequent handling of the complexes can be conducted in the atmosphere (even in the case of the $Fe^{2+}$ complex, which could be conceivably susceptible to oxidation,[16] it was established that the same compound is precipitated either in the atmosphere or by operating in a dry-nitrogen atmosphere and by using previously deoxygenated solvents). Analytical results (A. Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany) indicate that the complexes have the general empirical formula $M(puH)_2(ClO_4)_2{\cdot}3H_2O$ (Table I). Solubility characteristics are as follows. The complexes are readily soluble in *N,N*-dimethylformamide (DMF), with the exception of the $Zn^{2+}$ compound, which is rather sparingly soluble in this medium. The $Mn^{2+}$ and $Fe^{2+}$ complexes are soluble in water, while the $Mn^{2+}$ complex dissolves also in ethanol and is sparingly soluble in nitromethane; the rest of the new complexes are either sparingly soluble or insoluble in the preceding media. X-ray powder diffraction patterns indicate that all the complexes are either amorphous or characterized by a very low degree of crystallinity, at least in the powder form in which they were precipitated. Some attempts aimed at the recrystallization of the new complexes from DMF or ethanol were made but were not successful. Melting point determination experiments revealed that the complexes are initially discolored at 140–285 °C and then decompose without melting at 195–355 °C (Table I).

**Spectral, Magnetic, and Conductance Studies.** Infrared spectra (Table II) were obtained on KBr pellets (4000–500 $cm^{-1}$) and on Nujol mulls between high-density polyethylene windows (700–200 $cm^{-1}$), in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility, and molar conductivity ($10^{-3}$ M solutions in DMF at 25 °C) measurements (Table III) were obtained by using apparatus and techniques described elsewhere.[17,18] Magnetic susceptibility measurements at 300–80 K (Table IV) were obtained courtesy of Dr. A. B. P. Lever at York University, Toronto.

## Discussion

**Infrared and Conductance Data.** The molar condutivities of $10^{-3}$ M DMF solutions of the complexes indicate that these compounds behave as 1:2 electrolytes in solution,[19,20] involving exclusively ionic perchlorate. The $ClO_4$ groups are also ionic in the solid state, as clearly indicated by the single character of the $\nu_3$ and $\nu_4(ClO_4)$ fundamental vibrational modes[20,21] (Table II). With regard to the IR-inactive (for ionic $ClO_4^-$) $\nu_1$ and $\nu_2$ modes, ligand absorption in their respective regions (ca. 920 and 490–450 $cm^{-1}$) did not allow any conclusions as to whether they do appear as weak bands or not. It should be noted that comparisons of the IR spectra of the complexes herein reported to those of the corresponding metal chloride complexes with puH (currently under study) fully support the singlet character of the $\nu_3$ and $\nu_4(ClO_4)$ modes in the $M(puH)_2(ClO_4)_2{\cdot}3H_2O$ complexes and the masking of the $\nu_1$ and $\nu_2(ClO_4)$ regions by ligand bands; for instance a 1:1 complex of puH with $FeCl_2$ shows the following IR maxima in the regions of interest ($cm^{-1}$): 1220 m, sh, 1190 m, s, 1183 sh (A′ ($\delta_{CH}$)), 1132 w, 1109 m, 1101 m (A′ (R)), 1035 w; 961 m (A′ (R)), 919 m (A″ ($\gamma_{CH}$)); 666 w, 634 m (both A′ (R)), 608 m, 581 mw (both A″ (R)); 502 vw, 470 m (A″ (R)). The presence of aqua ligands is demonstrated by the appearance of the characteristic $\nu_{OH}$ absorption at 3420–3330 $cm^{-1}$ and

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(8) Weiss, R.; Venner, H. *Z. Chem.* **1967**, *7*, 428.

(9) Beck, W.; Kottmair, N. *Chem. Ber.* **1976**, *109*, 970.

(10) Weiss, R.; Venner, H. *Monatsber. Dtsch. Akad. Wiss. Berlin* **1971**, *13*, 199.

(11) Karpel, R. L.; Kustin, K.; Wolff, M. A. *Isr. J. Chem.* **1973**, *11*, 735; *J. Phys. Chem.* **1971**, *75*, 799.

(12) Fratiello, A.; Schuster, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1970**, *92*, 2304.

(13) Wang, S. M.; Li, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4592.

(14) Cheney, G. E.; Freiser, H.; Fernando, Q. *J. Am. Chem. Soc.* **1959**, *81*, 2611.

(15) Reinert, H.; Weiss, R. *Hoppe-Seyler's Z. Physiol. Chem.* **1969**, *350*, 1310.

(16) Behrens, N. B.; Goodgame, D. M. L.; Warnke, Z. *Inorg. Chim. Acta* **1978**, *31*, 257.

(17) Karayannis, N. M.; Mikulski, C. M.; Strocko, M. J.; Pytlewski, L. L.; Labes, M. M. *Inorg. Chim. Acta* **1974**, *8*, 91.

(18) Speca, A. N.; Pytlewski, L. L.; Karayannis, N. M. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1227.

(19) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(20) Farago, M. E.; James, J. M.; Trew, V. C. G. *J. Chem. Soc. A* **1967**, 820.

(21) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091.

**Table II.** Infrared Spectra (cm$^{-1}$) of M(puH)$_2$(ClO$_4$)$_2$·3H$_2$O Complexes[a]

| puH | M = Mn | M = Fe | M = Co | M = Ni | M = Cu | M = Zn | band assignt[b] |
|---|---|---|---|---|---|---|---|
| | 3330 vs, vb | 3340 vs, vb | 3400 vs, vb | 3370 vs, vb | 3415 vs, vb | 3420 vs, vb | $\nu_{OH}$(water) |
| 2725 s, b | 2670 m, b | 2690 m, b | 2680 m, b | 2695 m, b | 2700 m, vvb | 2685 m, vb | A′ im ($\nu_{NH}$) |
| 1613 vs | 1629 vs, 1602 s, sh | 1630 vs, 1600 s, sh | 1625 vs, sh, 1613 vs, 1600 s, sh | 1631 vs, 1619 vs, 1601 s, sh | 1639 vs, 1612 vs, 1603 vs, sh | 1647 vs, 1618 vs, 1602 vs, sh | A′ pym (8a) + $\delta_{H-O-H}$ |
| 1568 s | 1579 s | 1577 s | 1576 s, sh | 1580 s, b | 1585 vs, sh | 1590 vs, sh | A′ pym (8b) |
| 1499 w | 1482 m, sh | 1481 s | 1483 m, sh | *c* | 1484 m, sh | *c* | A′ im (R$_1$) |
| 1462 s | 1474 s | 1476 s | 1473 s | 1478 s, b | 1472 s | 1479 vs | A′ pym (19b) + im (R$_2$) |
| 1421 s | 1439 m, sh | 1440 s, sh | 1440 m, sh | *c* | *c* | *c* | A′ im (R$_3$) |
| 1398 vs | 1409 vvs | 1407 vvs | 1405 vvs | 1410 vvs | 1408 vvs | 1411 vvs | A′ pym (19a) |
| 1353 w | *c* | *c* | *c* | *c* | *c* | 1347 s | A′ pym (14) |
| 1329 s | 1332 s | 1331 s | 1330 s | 1332 s | 1329 s | 1320 s | A′ im (R$_4$) |
| 1308 w | 1305 ms | 1302 m | 1304 m | 1304 m | 1310 s | *c* | |
| 1267 vs | 1263 vs | 1261 vs | 1260 s | 1262 s | 1259 ms | 1263 ms | A′ im ($\delta_{NH}$) |
| 1241 sh | 1230 s | 1230 s | 1228 s | 1231 s | 1227 s | 1219 s, b | A′ ($\delta_{CH}$) |
| 1212 s | *c* | *c* | 1210 s | *c* | 1210 s, b | *c* | A′ ($\delta_{CH}$) |
| 1199 sh | 1197 s | 1193 s | 1192 s | 1199 m | 1197 s, b | 1193 s, sh | A′ ($\delta_{CH}$) |
| 1139 w | *c* | *c* | *c* | *c* | *c* | *c* | |
| | 1102 vvs, b | 1099 vvs, b | 1101 vvs, b | 1104 vvs, b | 1100 vvs, b | 1095 vvs, b | $\nu_3$(ClO$_4$) |
| 1093 s | *c* | *c* | *c* | *c* | *c* | *c* | A′ (R) |
| 1037 m, b | *c* | *c* | *c* | *c* | *c* | *c* | |
| 963 s | 960 m | 960 m | 960 m | 965 m | 963 w | 980 w, 960 w | A′ (R) |
| 938 m | *c* | *c* | *c* | *c* | *c* | *c* | |
| 922 m | 924 s | 921 s | 924 s | 927 s | 919 s | 928 s | A″ ($\gamma_{CH}$) |
| 904 s | *c* | *c* | *c* | *c* | *c* | 904 m, sh | A′ (R) |
| 861 w | 875 w | 870 w, b | 875 w, sh | 880 w, sh | 877 w, sh | 867 w, sh | A″ im ($\gamma_{NH}$) |
| 800 s | 800 s | 799 s | 798 s | 799 s | *c* | 800 s | A′ (R) |
| 786 m | 793 m, sh | 790 m, sh | 791 m, sh | *c* | 790 s | 791 s | A″ ($\gamma_{CH}$) |
| 720 w | 703 w, b | 698 w, b | 700 w, b | 698 w, b | 695 w | 695 w | |
| 651 w | 650 w, sh | 653 w, sh | 657 w, sh | 653 w, sh | 660 w | 670 w | A′ (R) |
| 635 m | 635 m, sh | 633 mw, sh | 631 mw, sh | *c* | 630 s | 635 s | A′ (R) |
| 621 w | 620 vs, vsp | 619 vs, vsp | 621 vs, vsp | 623 vs, vsp | 620 vs, vsp | 625 vs, vsp | A″ (R) + $\nu_4$(ClO$_4$) |
| 602 vs | 606 s, sh | 608 s, sh | 606 s, sh | 609 s, sh | 599 m, sh | 601 m, sh | A″ (R) |
| 564 m | 570 m, sh | 573 m, sh | 580 m, sh | 579 m, sh | 563 m | 570 ms | A″ (R) |
| 547 mw, sh | 550 w, sh | 549 w, sh | 553 w, sh | 550 w, b | 548 w, sh | 545 w, sh | |
| 510 w, b | 498 vw | 496 vw | 500 w | 502 w | 503 w | 504 m | |
| 447 m | 460 m | 459 m | 459 w | 466 w | 460 w | 466 m | A″ (R) |
| 413 w | 417 w | 415 w | 418 w | 417 w, sh | 420 w, sh | 416 w | A″ (R) |
| | 381 w | 393 w | 404 w | 421 w | 433 mw | 384 w | $\nu_{M-O}$(aqua) |
| 337 vw | 340 vw | 335 vw | 339 vw | 337 vw | 335 vw | 336 vw | |
| 310 vw, b | 305 vw | 311 vw | 312 vw | 302 vw | 307 vw | 304 vw | |
| 268 m | 279 m | 277 mw | 279 mw | 278 mw | 280 mw | 279 mw | A″ (R) |
| | 236 w, b, 208 m | 243 w, 209 w | 248 w, 233 w, 217 w, sh | 253 w, 237 w, 220 w | 256 w, 241 w, 222 w, sh | 229 w, b, 205 m | $\nu_{M-N}$ |
| 230 w | 228 w, sh | 231 w, sh | 229 w, sh | 230 w | 230 w | *c* | A″ (R) |
| 212 mw | 212 mw, sh | 210 w, sh | 211 w, sh | 214 w, sh | 215 w, sh | 213 w, sh | |

[a] Abbreviations: pym, pyrimidine; im, imidazole; R, ring skeletal vibration; s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder; sp, sharp. [b] puH band assignments after Lautié and Novak.[6,25] [c] Masked absorptions.

the identification of metal-sensitive bands, following the Irving–Williams series of wavenumber increase (i.e., Mn$^{2+}$ ~ Zn$^{2+}$ < Fe$^{2+}$ < Co$^{2+}$ < Ni$^{2+}$ < (Cu$^{2+}$) and attributable to $\nu_{M-O}$(aqua) modes.[22-24] The frequencies at which the latter absorptions occur are suggestive of hexacoordinated configurations (433–384 cm$^{-1}$).[22-24] Bands corresponding to the $\delta_{H-O-H}$, rocking and wagging modes of coordinated water[22,23] are presumably masked, in most cases, by the absorptions of the puH ligand.

Table II also shows the complete IR spectrum of puH at 1620–200 cm$^{-1}$ [6,25,26] (band assignments after Lautié and Novak[6,25]), along with the corresponding spectra of the new metal complexes. The possible participation of both pyrimidine (pym) and imidazole (im) nitrogens in coordination is suggested by shifts of several characteristic ring vibrational modes, attributable to both of these fragments of puH (e.g., A′ pym (8a), A′ pym (8b), and A′ pym (19a)[27] and A′ im R$_1$ and A′ im R$_3$[28]) upon metal complex formation.[6] On the other hand, the presence of the A′ im ($\nu_{NH}$) band at 2700–2670 cm$^{-1}$ in the spectra of the metal complexes ascertains the fact that neutral purine (puH) ligands are present in these compounds.[6] Finally, tentative $\nu_{M-N}$ assignments for metal-sensitive bands at 262–205 cm$^{-1}$ are in agreement with the trends of the Irving–Williams series and suggestive of a coordination number of 6 for the central metal ions.[16,29-32] The presence of up to three bands with possible $\nu_{M-N}$ character may be interpreted in terms of both terminal unidentate and bridging bidentate puH ligands in the first coordination sphere of each metal ion.[16,29-32]

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(22) Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* **1964**, *20*, 429.

(23) Ichida, K.; Kuroda, Y.; Nakamura, D.; Kubo, M. *Spectrochim. Acta, Part A* **1972**, *28A*, 2433. James, D. W.; Armishaw, R. F.; Frost, R. L. *Aust. J. Chem.* **1978**, *31*, 1401.

(24) Speca, A. N.; Gelfand, L. S.; Pytlewski, L. L.; Owens, C.; Karayannis, N. M. *Inorg. Chem.* **1976**, *15*, 1493.

(25) Lautié, A.; Novak, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1359.

(26) Willits, C. H.; Decius, J. C.; Dille, K. L.; Christensen, B. E. *J. Am. Chem. Soc.* **1955**, *77*, 2569.

(27) Foglizzo, R.; Novak, A. *Spectrochim. Acta, Part A* **1970**, *26A*, 2281. Zarembowitch, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1976**, *73*, 407.

(28) Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1451. Eilbeck, W. J.; Holmes, F.; Underhill, A. E. *J. Chem. Soc. A* **1967**, 757.

(29) Guichelaar, M. A.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 295.

(30) Ferraro, J. R.; Zipper, J.; Wozniak, W. *Appl. Spectrosc.* **1969**, *23*, 160.

(31) Goldstein, M.; Taylor, F. B.; Unsworth, W. D. *J. Chem. Soc., Dalton Trans.* **1972**, 418. Goldstein, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 567.

(32) Chasan, D. E.; Pytlewski, L. L.; Owens, C.; Karayannis, N. M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1799; **1977**, *39*, 1137.

**Table III.** Solid-State (Nujol Mull) Electronic Spectra, Magnetic Susceptibilities,[a] and Molar Conductivities ($10^{-3}$ M DMF Solutions at 25 °C) of $M(puH)_2(ClO_4)_2\cdot 3H_2O$ Complexes

| M | $\lambda_{max}$,[b,c] nm | $10^6\chi_M^{cor}$, cgsu | $\mu_{eff}$, $\mu_B$ | $\Lambda_M$, $\Omega^{-1}$ $cm^2$ $mol^{-1}$ |
|---|---|---|---|---|
| Mn | 218 vvs, 223 vvs, 247 vs, 281 vs, b, 344 s, sh, (1120 w, b), (1290 w, b) | 15 344 | 6.07 | 143 |
| Fe | 208 vvs, 213 vvs, 254 vs, 284 vs, 344 s, sh, 415 s, sh, 730 ms, b, 920 m, b, (1140 w, vb), (1280 w, vb) | 10 161 | 4.94 | 152 |
| Co | 203 vvs, 221 vvs, sh, 253 vs, 278 vs, b, 345 s, sh, 467 ms, sh, 523 m, 550 m, 700 m, sh, 924 mw, b, 1175 mw, b, (1300 w, vb) | 10 411 | 4.98 | 147 |
| Ni | 206 vvs, 211 vvs, 257 vs, sh, 282 vs, 350 s, sh, 397 s, sh, 435 m, sh, 645 m, b, 710 m, b, 965 mw, b, 1040 mw, b, (1140 w, vb), (1300 w, vvb) | 3 660 | 2.94 | 155 |
| Cu | 224 vvs, 230 vvs, 266 vs, 290 vs, 347 s, sh, 556 m, sh, 585 ms, b, 777 m, b, (1130 w, vb), (1280 w, vvb) | 1 767 | 2.05 | 166 |
| Zn | 202 vvs, 209 vvs, 219 vvs, 253 vs, 278 vvs, b, 342 s, sh, (1130 w, b), (1290 w, vb) | diamagnetic | | 138 |

[a] Determined at 298 K for M = Mn, Fe, and Zn at these laboratories and at 297 K for M = Co and Cu and 295 K for M = Ni, courtesy of Dr. Lever. [b] UV spectrum (nm) of puH (Nujol mull): 188 vvs, 204 vvs (both $A_{1g} \rightarrow E_{1u}$), 252 vs ($A_{1g} \rightarrow B_{1u}$), 267 vs ($A_{1g} \rightarrow B_{2u}$), 293 s, sh ($n \rightarrow \pi^*$), 345 m, sh; $\pi \rightarrow \pi^*$ (188–267 nm) and $n \rightarrow \pi^*$ transition band assignments are after Clark and Tinoco.[33] [c] Near-IR bands, common in the spectra of all the metal complexes and apparently due to vibrational overtones and combination modes originating from puH,[29] are shown in parentheses; near-IR bands (nm) of uncomplexed puH: 1155 vw, vvb, 1350 vw, vvb.

**Table IV.** Magnetic Behavior of the New $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ Complexes at 300–80 K

| M = Co | | | M = Ni | | | M = Cu | | |
|---|---|---|---|---|---|---|---|---|
| *T*, K | $10^6 \times \chi_M^{cor}$, cgsu | $\mu_{eff}$, $\mu_B$ | *T*, K | $10^6 \times \chi_M^{cor}$, cgsu | $\mu_{eff}$, $\mu_B$ | *T*, K | $10^6 \times \chi_M^{cor}$, cgsu | $\mu_{eff}$, $\mu_B$ |
| 79.7 | 32 103 | 4.52 | 79.9 | 11 402 | 2.70 | 88.5 | 4496 | 1.78 |
| 106.3 | 25 575 | 4.67 | 89.9 | 10 602 | 2.76 | 110.3 | 3724 | 1.81 |
| 132.8 | 21 607 | 4.79 | 114.5 | 8511 | 2.79 | 143.8 | 3061 | 1.88 |
| 159.0 | 18 541 | 4.86 | 130.3 | 7558 | 2.81 | 179.5 | 2604 | 1.93 |
| 185.2 | 16 144 | 4.89 | 164.0 | 6058 | 2.82 | 213.7 | 2193 | 1.94 |
| 209.4 | 14 415 | 4.92 | 187.9 | 5515 | 2.88 | 241.4 | 2071 | 2.00 |
| 235.9 | 12 804 | 4.92 | 203.6 | 5114 | 2.89 | 259.0 | 1970 | 2.02 |
| 271.1 | 11 313 | 4.95 | 230.9 | 4568 | 2.91 | 278.1 | 1842 | 2.02 |
| 297.0 | 10 411 | 4.98 | 254.8 | 4167 | 2.92 | 296.5 | 1767 | 2.05 |
| | | | 278.4 | 3878 | 2.94 | | | |
| | | | 295.2 | 3660 | 2.94 | | | |

**Electronic Spectra and Magnetic Moments.** The UV bands of puH[33,34] show the following changes upon metal complex formation. The $\pi \rightarrow \pi^*$ transition bands at 188–204 and 267 nm undergo sizeable shifts to lower energies, while the $\pi \rightarrow \pi^*$ absorption at 252 nm seems to be, with one exception (M = Cu), rather insensitive to metal complex formation. The $n \rightarrow \pi^*$ transition at 293 nm is generally masked by the shifted low-energy $\pi \rightarrow \pi^*$ absorption, whereas the shoulder at 345 nm is observed in the spectra of all the new compexes. Near-IR bands of puH, presumably due to vibrational overtones and combination modes,[29] appear shifted in the spectra of the metal complexes; these bands are shown in parentheses in Table III. Strong metal-to-ligand charge-transfer absorption,[35] originating in the UV and trailing off into the visible region, is also observed in the spectra of the new paramagnetic complexes. The d–d transition spectra of the $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ complexes are generally characterized by obvious splittings of the d–d bands (Table III); these splittings can be attributed to low-symmetry hexacoordinated configurations.[36] Band assignments (in pure $O_h$ symmetry) are as follows:[36–38] for M = Fe ($^5T_{2g} \rightarrow {}^5E_g$) 730, 920; for M = Co ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4A_{2g}(F)$) 467, 523, 550; for M = Cd ($^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) 924, 1170 (the band at 700 nm may be due to a transition to the $^2G$ level); for M = Ni ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$) 397, 435; ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^1E_g(D)$) 645, 710; ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$) 965, 1040; for M = Cu ($^2E_g \rightarrow {}^2T_{2g}$) 556, 585, 777 nm. Approximate *Dq* values calculated for the $Fe^{2+}$ (1212 $cm^{-1}$) and $Ni^{2+}$ (998 $cm^{-1}$) complexes seem reasonable for $MN_3O_3$ chromophores. Thus, for instance, $[ML_3](ClO_4)_2$ chelates with 2,2′-bipyridine *N*-oxide, also involving $MN_3O_3$ absorbing species, have *Dq* values of 1160 $cm^{-1}$ for M = Fe and 1029 $cm^{-1}$ for M = Ni,[38] whereas for a number of 9-methyladenine (ma) $Ni^{2+}$ complexes with $NiN_2O_4$ chromophores the following *Dq* values were observed: $[Ni(ma)_2(OH_2)_2(ONO_2)_2]$, 960 $cm^{-1}$;[29] $[Ni(ma)_2(OH_2)_4]X_2$ (X = Cl, Br), 980 $cm^{-1}$.[16] It should be also pointed out that the d–d spectrum of the $Cu^{2+}$ complex, with the main maximum at 585 nm and a weaker band at 777 nm, is very similar to that of $Cu(ma)_2(NO_3)_2\cdot H_2O$ and suggestive of a coordination number of 6.[29]

The ambient-temperature magnetic moments of the metal(II) perchlorate complexes of puH (Table III) are generally normal for high-spin $3d^5$–$3d^8$ compounds or the $3d^9$ configuration.[39] Since the biologically important purines have the tendency to function as bidentate bridging ligands,[2,3] a temperature-dependence study of the paramagnetism of the new complexes seemed appropriate. Magnetic data at 300–80 K, shown in Table IV, were collected for the $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ complexes, which were available in sufficient quantities. In all three cases, a significant decrease of the magnetic moment (by 0.24–0.46 $\mu_B$) was observed as the temperature was lowered from 295–297 to 80–89 K. Plots of $1/\chi_M$ vs. *T* show that the Curie–Weiss law is obeyed in the 300–110 K region, and the Weiss constants corresponding to the linear portions of the plots are $\Theta = -3$, $-19$, and $-76$ K for M = Co, Ni, and Cu, respectively. At temperatures below 110 K, the $1/\chi_M$ vs. *T* plots for the $Co^{2+}$ and $Ni^{2+}$ complexes show small deviations from Curie–Weiss behavior, suggestive of antiferromagnetic exchange interactions.[40] On the other hand, the corresponding plot for the $Cu^{2+}$ complex shows also a deviation from Curie–Weiss behavior but in the opposite direction to that expected for an antiferromagnetic situation. A number of polynuclear $Cu^{2+}$ complexes with such ligands as nucleosides[41] and triazoles[42] have been recently found to behave in a similar

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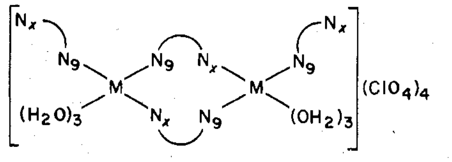
(33) Clark, L. B.; Tinoco, I., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 11.
(34) Kwiatkowski, J. *Mol. Phys.* **1967**, *12*, 197. Chen, H. H.; Clark, L. B. *J. Chem. Phys.* **1969**, *51*, 1862.
(35) Lever, A. B. P.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1962**, 1235; **1963**, 3156, 5042; **1964**, 1187, 4761.
(36) Byers, W.; Lever, A. B. P.; Parish, R. V. *Inorg. Chem.* **1968**, *7*, 1835.
(37) Lever, A. B. P.; Ogden, D. *J. Chem. Soc. A* **1967**, 2041.
(38) Speca, A. N.; Karayannis, N. M.; Pytlewski, L. L.; Winters, L. J.; Kandasamy, D. *Inorg. Chem.* **1973**, *12*, 1221.
(39) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.
(40) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225. Chasan, D. E.; Pytlewski, L. L.; Owens, C.; Karayannis, N. M. *Chem. Chron.* **1979**, *8*, 53.
(41) Nelson, H. C.; Villa, J. F. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1643; **1980**, *42*, 133.
(42) Lynch, M.; Hyde, K. E.; Bocko, P. L.; Kokoszka, G. F. *Inorg. Chem.* **1977**, *16*, 562.

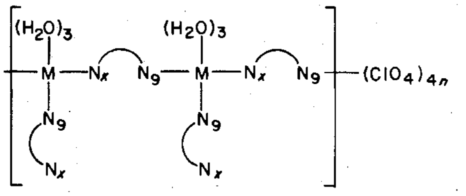
manner, showing exchange in the ferromagnetic direction at low temperatures.[41,42] Although additional magnetic studies, covering the 80–4.2 K region, would be necessary for the complete understanding of the magnetic exchange interactions in the new complexes, the overall magnetic evidence currently available ($\mu_{\text{eff}}$ decreases with temperature, negative $\Theta$ values, and deviation from Curie–Weiss behavior at low temperatures) is clearly in favor of bi- or polynuclear rather than monomeric configurations for these compounds.[40-42]

**Conclusion.** On the basis of the evidence presented, it appears that the new metal complexes are generally hexacoordinated, involving $MN_3O_3$ moieties. One of the puH ligands acts as a bidentate while the second is unidentate. The limited solubility of the metal complexes in organic media, combined with their magnetic behavior and the fact that purines do not seem to have any pronounced tendency to function as bidentate chelating agents,[2,3] is in favor of bi- or oligonuclear structures. With regard to the possible bonding sites of puH, it should be mentioned that, among various biologically interesting purines, adenine, guanine, and xanthine show a pronounced tendency to use the N(9) site in coordination,[2,43-47] but theophylline seems to prefer coordination through the N(7) site.[48,49] When functioning as bidentate, bridging, and N,N bonded, these ligands seem to always coordinate through the N(9) nitrogen, involving either N(3),N(9) (in complexes with either neutral or monodeprotonated purines)[2,43-45] or N(7),N(9) (in some monodeprotonated purine complexes)[50,51] bonding. N(1),N(7) bonding has been established only for complexes with 9-substituted purines (e.g., 9-methyladenine (ma)).[52,53] Free puH exists in the N(7)-protonated form (I) in the crystal, with the 7H-purine planar molecules joined together in infinite chains by relatively short (2.85 Å) N(7)–H···N(9) hydrogen bonds.[54] It seems reasonable to assume that coordinated puH remains in the N(7)-protonated form. Among the remaining three nitrogen sites, N(9) is the most and N(3) is the least inclined to coordinate.[2] On the other hand, coordination of purines as bidentate, bridging, and N(3),N(9) bonded has been established for several bi- or polynuclear $Cu^{2+}$ complexes,[2,43-45] while complexes involving N(1),N(9)-bonded, bridging purines have not been elucidated, at least so far.

In light of the preceding discussion, it is considered as likely that N(9) is the bonding site of the terminal unidentate puH, as well as one of the bonding sites of the bridging bidentate puH ligand in the new complexes. As regards the second bonding site of the bidentate purine groups, no distinction between N(1) and N(3) can be made at this point. Di-,tri- and polymeric (linear or cross-linked) structures have been established[2,43-45,50] or postulated[41] for various metal ($Cu^{2+}$ in most cases) complexes with purine bases and nucleosides. It is obvious that a variety of ligand-bridged structural types can be proposed. While not dismissing other possibilities, two relatively simple possible linear structural types are discussed here, viz., a double-bridged dimer of type II and a single-bridged oligomer of type III ($\overset{\frown}{N_x N_9}$ ($x$ = 1 or 3), 7H-purine, with only the ligand sites shown for simplicity, M = Mn, Fe, Co, Ni, Cu, Zn). Structural type III is considered as being more likely than II, especially since the presence of double- or multiple-ligand bridges in $Cu^{2+}$ complexes usually results in subnormal room-temperature magnetic moments (below 1.6 $\mu$B) and clear-cut deviation from Curie–Weiss behavior, even at relatively high temperatures.[55-58] Complexes of this type include several well-characterized $Cu^{2+}$ dimers with quadruple adenine bridges,[56-58] whereas linear single-bridged polymeric $Cu^{2+}$ complexes with bridging bidentate N,N ligands (e.g., *p*-diazines and purine derivatives) or hydroxyl groups are quite often characterized by normal or near-normal ambient-temperature magnetic moments and show evidence favoring magnetic exchange interactions only at low temperatures.[30,41,59,60]



II



III

Prior to conclusion, it should be mentioned that several 3d metal complexes with 9-methyladenine, involving exclusively terminal unidentate ma ligands, have been prepared from ethanol, e.g., $[M(ma)_2(OH_2)_2(ONO_2)_2]$ (M = Co, Ni)[29] and $[Ni(ma)_2(OH_2)_4]Cl_2\cdot 2H_2O$.[16] Our preparative method involved the use of teof, an effective dehydrating agent,[61] along with ethanol as the preparation medium. Although the use of teof did not result in the isolation of anhydrous complexes, it has apparently limited the number of water molecules available for coordination and forced one of the two puH ligands to act as a bidentate bridging group, so that a coordination number of 6 be attained.

**Registry No.** $Mn(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-75-0; $Fe(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-77-2; $Co(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-79-4; $Ni(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-81-8; $Cu(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-83-0; $Zn(puH)_2(ClO_4)_2\cdot 3H_2O$, 74868-85-2.

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(43) de Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2400.

(44) Sletten, E. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1480.

(45) Terzis, A.; Beauchamp, A. L.; Rivest, R. *Inorg. Chem.* **1973**, *12*, 1166.

(46) Carrabine, J. A.; Sundaralingam, S. *J. Am. Chem. Soc.* **1970**, *92*, 369; *Biochemistry* **1971**, *10*, 292. Sundaralingam, S.; Carrabine, J. A. *J. Mol. Biol.* **1971**, *61*, 287.

(47) Marzilli, L. G.; Epps, L. A.; Sorrell, T.; Kistenmacher, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 3351.

(48) Kistenmacher, T. J.; Szalda, D. J.; Chiang, C. C.; Rossi, M.; Marzilli, L. G. *Inorg. Chem.* **1978**, *17*, 2582.

(49) Biagini-Cingi, M.; Manotti-Lanfredi, A. M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 221.

(50) Prizant, L; Olivier, M. J.; Rivest, R.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 2765.

(51) Agnew, N. H.; Appleton, T. G.; Hall, J. R.; Kilmister, J. F.; McMahon, I. J. *J. Chem. Soc., Chem. Commun.* **1979**, 324.

(52) de Meester, P.; Goodgame, D. M. L.; Skapski, A. C.; Warnke, Z. *Biochim. Biophys. Acta* **1973**, *324*, 301.

(53) Lock, G. J. L.; Speranzini, R. A.; Turner, G.; Powell, J. *J. Am. Chem. Soc.* **1976**, *98*, 7865.

(54) Watson, D. G.; Sweet, R. M.; Marsh, R. E. *Acta Crystallogr.* **1965**, *19*, 573.

(55) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. Watson, W. H. *Inorg. Chem.* **1969**, *8*, 1879.

(56) Goodgame, D. M. L.; Price, K. A. *Nature (London)* **1968**, *220*, 783. Duerst, R. W.; Baum, S. J.; Kokoszka, G. F. *Ibid.* **1969**, *222*, 661.

(57) Jezowska-Trzebiatowska, B.; Kozlowski, H.; Antonów, A. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1974**, *22*, 31. Hanson, M. V.; Smith, C. B.; Simpson, G. D.; Carlisle, G. O. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 225.

(58) Brown, D. B.; Hall, J. W.; Helis, H. M.; Walton, E. G.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2675.

(59) Campbell, M. J. M.; Grzeskowiak, R.; Taylor, F. B. *J. Chem. Soc. A* **1970**, 19. Hyde, K.; Kokoszka, G. F.; Gordon, G. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1993.

(60) Brown, D. B.; Wasson, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2556. Richardson, H. W.; Hatfield, W. E. *J. Am. Chem. Soc.* **1976**, *98*, 835.

(61) van Leeuwen, P. W. N. M.; Groeneveld, W. L. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 145.