(ii) Both $[(C_6H_5N)PCl]_2$ (**5**) and $[(t\text{-}C_4H_9N)PCl]_2$ (**17**)[7] are thermodynamically stable as cis isomers.[2] In neither case has evidence for a trans isomer been obtained. Apparently, the *cis* Cl–$PN_2P$–Cl ring unit is sufficiently stable that replacement of *N*(ring)-$C_6H_5$ with *t*-$C_4H_9$ groups is not electronically or sterically significant enough to cause a change in isomer preference.

(iii) The $P_2N_2$ rings of the *cis-N*(ring)-aryldiazadiphosphetidines X-ray crystallographically characterized so far (**3**[6], **4**[19] and **5**) are planar or nearly planar. In contrast, the $P_2N_2$ rings of *cis-N*-(ring)-alkyldiazadiphosphetidines are puckered,[5] bent so as to increase the exo-substituent intramolecular distances. This stabilization of a $P_2N_2$ ring could arise through aryl group $\pi$ interaction with p orbitals of the ring nitrogen atoms. Because the *N*(ring)-aryl-substituted $P_2N_2$ rings pucker only slightly to allow minimization of endo–exo- or exo–exo-group interactions,[5] their ground-state energies may be increased relative to those of the trans isomers and relative to those of cis-*N*(ring)-alkyl-substituted compoounds. This effect, in systems with large exo groups (e.g. **6**, **10–16**), could ultimately cause cis isomers to become less stable than the trans forms.

(iv) Trans isomers are favored for $[(C_6H_5N)PN(C_2H_5)_2]_2$ (**11**) and the series **13–16**. In contrast, the *N*(ring)-alkyl analogues $[(t\text{-}C_4H_9N)PN(CH_3)_2]_2$ (**18**) and $[(t\text{-}C_4H_9N)PN(C_2H_5)_2]_2$ (**19**) prefer the cis form. Since the *t*-$C_4H_9$ groups are bulkier than the $C_6H_5$ units, this result appears *contra* steric. However, this paradox might arise because the $P_2N_2$ ring in **11** and **13–16** does not pucker and yield a stable cis form. In **18** and **19**, ring puckering allows relief of exo-group–endo-group repulsion and causes the assumption of the stable cis isomeric form.

The results obtained so far suggest that *N*(ring)-aryldiazadiphosphetidine isomer preference is more sensitive to exo-group substitution than are the *N*(ring)-alkyl-substituted analogues. This might be related to the tendency toward $P_2N_2$ ring planarity in *N*(ring)-aryl systems vs. nonplanarity in the *N*-(ring)-alkyl compounds. This possibility is being investigated further currently.

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**Supplementary Material Available:** Listings of observed and calculated structure factors, thermal and positional parameters, derived and rigid group positional and thermal parameters, and equations of planes and atom derivations from planes (11 pages). Ordering information is given on any current masthead page.

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(40) Thompson, M. L.; Haltiwanger, R. C.; Norman, A. D., submitted for publication.

(41) Hill, T. G.; Haltiwanger, R. C.; Norman, A. D., submitted for publication.

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# Coordination Compounds of a Pentadentate Pyrazole Derivative of Diaminopropane. Crystal Structure of Aqua(*N*,*N*,*N'*-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane)cobalt(II) Diperchlorate Hydrate, $[Co(ap3d)(H_2O)](ClO_4)_2{\cdot}H_2O$

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Coordination compounds of the type $M(ap3d)(anion)_2(H_2O)_x$ are described in which M is one of the divalent metals Co, Ni, Cu, and Zn, the anion is $ClO_4^-$ and $BF_4^-$, ap3d stands for $C_{21}H_{34}N_8$ or *N*,*N*,*N'*-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane, and $x = 1\text{–}3$. The compounds have been characterized by several analytical techniques and spectroscopic methods. In all compounds the ligand is pentadentate. The six-coordination is completed by one water molecule. The coordination geometry is distorted-octahedral as deduced from ligand field spectra for Co(II), Ni(II), and Cu(II) and powder isomorphism within this group. The noncoordinating water molecules are hydrogen bonded to the anions. The compound $[Co(ap3d)(H_2O)](ClO_4)_2{\cdot}H_2O$ crystallizes in the space group $P2_1/n$ (monoclinic) with $a = 16.927$ (4) Å, $b = 18.853$ (4) Å, $c = 9.926$ (7) Å, $\beta = 102.02$ (3)°, and $Z = 4$. The structure has been solved by heavy-atom techniques and refined by least-squares methods to a residual *R* value of 0.050 ($R_w = 0.057$). The coordination geometry around the Co(II) ion can be described as a distorted octahedron formed by the five nitrogen atoms of the ligand ap3d and a water molecule. The bonding distances are about 2.1 Å. A second water molecule is hydrogen bonded to the coordinated water molecule and to the perchlorate ions.

## Introduction

As part of a research program on the synthesis and structure of coordination compounds modeling the active site in metalloproteins we reported a novel method for the synthesis of N-substituted pyrazole chelates and a number of their coordination compounds.[1-5] One of the factors governing the properties of a metalloprotein is the steric constraint exerted by the protein on the active site containing the metal ion. Seven-coordinate compounds of the pyrazole derivative of 1,2-diaminoethane have been reported[5] with unusually long metal–nitrogen distances, their geometry being described as bicapped-octahedral. To verify whether only sterical factors are involved in producing this unusual coordination geometry, a study of the coordination behavior of a pyrazole derivative of 1,3-diaminopropane has been undertaken. Several coordination compounds of *N*,*N*,*N'*-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane (ap3d) have been synthesized, and the crystal structure of $[Co(ap3d)(H_2O)](ClO_4)_2{\cdot}H_2O$ has been solved.

## Experimental Section

The compound *N*,*N*,*N'*-tris((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane (ap3d) was synthesized by the condensation of 1,3-diaminopropane and *N*-(hydroxymethyl)-3,5-dimethylpyrazole in acetonitrile as described by Driessen.[1]

All other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

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(3) Blonk, H. L.; Driessen, W. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1699.

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**Table I.** Fractional Coordinates (Co, ×10$^5$; Others, 10$^4$) and Isotropic Thermal Parameters (Co, Cl, and O(91), ×10$^2$ Å$^2$; Others, ×10 Å$^2$) of the Non-Hydrogen Atoms in $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$[a]

| atom | $x/a$ | $y/b$ | $z/c$ | $B_{iso}$[b] |
|---|---|---|---|---|
| Co(1) | 21371 (5) | 16952 (5) | 36987 (9) | 346 (2) |
| N(2) | 2308 (3) | 2524 (3) | 5372 (5) | 37 (2) |
| C(3) | 1761 (4) | 2514 (4) | 6352 (7) | 49 (2) |
| C(4) | 1387 (6) | 1856 (5) | 6596 (9) | 115 (4) |
| C(5) | 898 (4) | 1411 (4) | 5597 (6) | 51 (2) |
| N(6) | 1268 (3) | 1126 (3) | 4543 (5) | 64 (2) |
| C(10) | 3151 (4) | 2423 (3) | 6073 (7) | 46 (2) |
| N(11) | 3290 (3) | 1675 (3) | 6304 (5) | 44 (2) |
| N(12) | 3057 (3) | 1227 (3) | 5206 (5) | 43 (2) |
| C(13) | 3320 (4) | 589 (4) | 5663 (7) | 46 (2) |
| C(14) | 3713 (4) | 632 (4) | 7049 (7) | 53 (2) |
| C(15) | 3693 (4) | 1323 (4) | 7429 (6) | 47 (2) |
| C(16) | 3208 (5) | −41 (4) | 4756 (8) | 62 (3) |
| C(17) | 4034 (4) | 1719 (5) | 8730 (7) | 68 (3) |
| C(20) | 2207 (4) | 3202 (3) | 4596 (7) | 48 (2) |
| N(21) | 1502 (3) | 3138 (3) | 3487 (5) | 40 (2) |
| N(22) | 1372 (3) | 2512 (3) | 2764 (5) | 39 (2) |
| C(23) | 764 (4) | 2656 (4) | 1704 (6) | 39 (2) |
| C(24) | 530 (4) | 3365 (4) | 1741 (7) | 46 (2) |
| C(25) | 1009 (4) | 3656 (4) | 2887 (7) | 45 (2) |
| C(26) | 441 (4) | 2094 (4) | 680 (7) | 55 (2) |
| C(27) | 1028 (5) | 4381 (3) | 3480 (7) | 57 (3) |
| C(30) | 756 (5) | 788 (5) | 3444 (7) | 69 (6) |
| C(30′) | 911 (5) | 530 (5) | 3836 (7) | 46 (5) |
| N(31) | 1261 (3) | 427 (3) | 2592 (5) | 45 (2) |
| N(32) | 1818 (3) | 880 (3) | 2246 (5) | 40 (2) |
| C(33) | 1995 (4) | 610 (4) | 1108 (6) | 44 (2) |
| C(34) | 1556 (5) | −4 (4) | 753 (7) | 62 (3) |
| C(35) | 1088 (4) | −166 (4) | 1695 (7) | 54 (2) |
| C(36) | 2572 (5) | 953 (4) | 402 (7) | 67 (3) |
| C(37) | 497 (6) | −671 (5) | 1830 (10) | 91 (4) |
| O(91) | 3045 (3) | 2200 (2) | 2841 (4) | 523 (15) |
| O(92) | 2513 (4) | 3006 (4) | 513 (6) | 106 (3) |
| Cl(7) | 5109 (1) | 1426 (1) | 2687 (2) | 604 (7) |
| O(71) | 5849 (3) | 1620 (3) | 3562 (5) | 75 (2) |
| O(72) | 5241 (4) | 995 (3) | 1602 (5) | 91 (2) |
| O(73) | 4626 (5) | 1075 (6) | 3436 (7) | 169 (4) |
| O(74) | 4717 (4) | 2045 (4) | 2166 (8) | 141 (3) |
| Cl(8) | 3550 (1) | 4180 (1) | −1886 (2) | 733 (8) |
| O(81) | 3749 (7) | 4874 (4) | −1793 (9) | 176 (5) |
| O(82) | 3992 (5) | 3878 (4) | −2749 (8) | 134 (3) |
| O(83) | 2759 (5) | 4058 (5) | −2448 (9) | 170 (4) |
| O(84) | 3733 (6) | 3888 (6) | −630 (8) | 177 (5) |

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] $B_{iso} = {}^8/_3\pi^2$ trace $\tilde{U}$.

**Table II.** Selected Interatomic Distances (Å) for $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$

| | | | |
|---|---|---|---|
| Co(1)–N(2) | 2.255 (5) | Co(1)–N(22) | 2.099 (5) |
| Co(1)–N(6) | 2.129 (5) | Co(1)–N(32) | 2.100 (5) |
| Co(1)–N(12) | 2.115 (5) | Co(1)–O(91) | 2.129 (4) |

**Table III.** Selected Bond Angles (deg) for $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$

| | | | |
|---|---|---|---|
| N(22)–Co(1)–N(32) | 100.8 (2) | N(2)–Co(1)–N(6) | 93.0 (2) |
| N(22)–Co(1)–O(91) | 85.7 (2) | N(6)–Co(1)–N(22) | 97.5 (2) |
| N(12)–Co(1)–O(91) | 89.0 (2) | N(2)–Co(1)–N(12) | 78.8 (2) |
| N(2)–Co(1)–O(91) | 89.6 (2) | N(2)–Co(1)–N(22) | 77.9 (2) |
| N(32)–Co(1)–O(91) | 99.0 (2) | N(6)–Co(1)–N(12) | 88.8 (2) |
| N(12)–Co(1)–N(32) | 103.1 (2) | N(6)–Co(1)–N(32) | 78.5 (2) |
| N(2)–Co(1)–N(32) | 171.2 (2) | N(6)–Co(1)–O(91) | 176.3 (2) |
| N(12)–Co(1)–N(22) | 156.1 (2) | | |

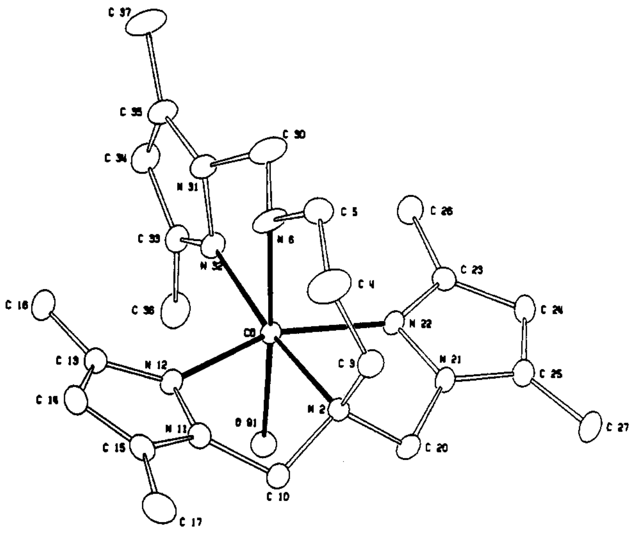

**Figure 1.** ORTEP projection and atomic labeling of $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$. The perchlorate anions, the second water molecule, and the hydrogen atoms are omitted for clarity.

*Caution*! Some compounds in this work contain perchlorate anions. Although no accidents with perchlorates occurred during the experimental work for this article, it should be pointed out that perchlorates are hazardous because of the possibility of explosion. See also ref 12.

The coordination compounds were prepared by dissolving the hydrated metal salts (3 mmol) in 25 mL of warm ethanol and adding the solutions to warm solutions of the ligand ap3d (3 mmol) in 25 mL of ethanol. After the solutions were cooled to room temperature and in some cases after evaporation of part of the solvent, solid compounds formed that were collected on a filter, washed with a little diethyl ether, and dried at room temperature. Single crystals of $[Co(ap3d)(H_2O)](ClO_4)_2 \cdot H_2O$ suitable for X-ray diffraction were obtained by dissolving the microcrystalline solid in ethanol and subsequently slowly evaporating part of the solvent. These crystals appeared to be unstable in the air; therefore, a single crystal was mounted in a glass capillary with a little of the mother liquor, which was supported with a small piece of paper tissue.

Metal analyses were carried out complexometrically with EDTA as the complexing agent.[6] C, H, and N analyses were carried out by University College, Department of Chemistry, Dublin, Ireland.

Physical measurements were performed on equipment described elsewhere.[5]

**Crystal data**: $C_{21}H_{38}N_8O_{10}Cl_2Co$, $M_r$ = 692.42, monoclinic, space group $P2_1/n$, $a$ = 16.927 (4) Å, $b$ = 18.853(4) Å, $c$ = 9.926 (7) Å, $\beta$ = 102.02 (3)°, $V$ = 3098.3 Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.48 g·cm$^{-3}$, $F(000)$ = 1442.55, $\mu$(Mo K$\alpha$) = 7.81 cm$^{-1}$, $\lambda$(Mo K$\alpha$) = 0.71073 Å.

**Data Collection and Structure Refinement.** A single crystal of approximate dimensions 0.68 × 0.20 × 0.08 mm, mounted in a glass capillary supported with the mother liquor on a paper tissue, was used for data collection. Cell dimensions were determined by least-squares refinement from the measured setting angles of 24 reflections ($10 < \theta < 12°$). X-ray intensities were collected on a four-circle Enraf-Nonius diffractometer at room temperature by the $\omega$–$\theta$ scan technique for $2 < \theta < 20°$ with $-16 \le h \le 16$, $0 \le k \le 18$, and $-9 \le l \le 9$, with use of graphite-monochromatized Mo K$\alpha$ radiation.

In total 6010 reflections were measured, of which 3012 were independent: from these independent reflections there were 2065 reflections, with $I > 2\sigma(I)$, considered as observed and used in the refinement. Intensities were corrected for Lorentz and polarization effects. Absorption correction was not necessary. The calculations were performed on the Leiden University Amdahl V7B computer using a local set of computer programs. Scattering factors and anomalous dispersion corrections were taken from ref 7. The structure was solved by the heavy-atom technique and refined by block-matrix least-squares calculations. Some hydrogen atoms were located from difference-Fourier maps; others were placed at 0.95 Å from the parent atoms. The thermal parameters of the hydrogen atoms were refined, while coupled to each other, with a final value of 9.77 Å$^2$. The positional parameters of the hydrogen atoms were refined with the atoms coupled to the parent atoms. The thermal parameters of the non-hydrogen atoms were anisotropically refined. The function minimized was $\sum w||F_o| - |F_c||^2$ with $w = 1/\sigma^2(F)$. At the final stage the conventional discrepancy index $R_F = \sum(||F_c| - |F_o||)/\sum|F_o|$ had been reduced to 0.050 and the weighted factor $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 0.057.

For the non-hydrogen atoms the atomic coordinates and the isotropic thermal parameters are listed in Table I. Bond distances are given in

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(6) Vogel, A. I. "Quantitative Inorganic Analysis"; Longmans Green and Co.: London, 1961.

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

**Table IV.** Colors, X-ray and Infrared Types, and Electronic Absorption Data of the Coordination Compounds of the Ligand ap3d

| | X-ray[a] | IR[d] | electronic abs (powder reflectance)[b] | color |
|---|---|---|---|---|
| $[Co(ap3d)(H_2O)](BF_4)_2\cdot 2H_2O$ | A | I | 9.44, 20.3 | brick red |
| $[Ni(ap3d)(H_2O)](BF_4)_2\cdot 2H_2O$ | A | I | 10.50, 16.9, 27.3 | light blue |
| $[Cu(ap3d)(H_2O)](BF_4)_2$ | B | II | 13.16 (sh 10.2)[c] | blue |
| $[Zn(ap3d)(H_2O)](BF_4)_2$ | C | III | | white |
| $[Co(ap3d)(H_2O)](ClO_4)_2\cdot H_2O$ | D | I′ | 9.43, 21.05 | brick red |
| $[Ni(ap3d)(H_2O)](ClO_4)_2$ | E | I″ | 10.38, 16.8, 27.0 | light blue |
| $[Cu(ap3d)(H_2O)](ClO_4)_2$ | B | II′ | 15.0 (sh 9.9)[c] | blue |
| $[Zn(ap3d)(H_2O)](ClO_4)_2$ | F | III′ | | white |

[a] Structural isomorphism based on powder diffraction patterns. [b] Frequencies in $10^3$ cm$^{-1}$. [c] The differences in the electronic absorption spectra of the copper compounds in spite of their powder and IR isomorphism are explained in Spectroscopic Results. [d] The primes denote slight differences in anion and water vibration frequencies.

Table II and bond angles in Table III. An ORTEP[8] drawing of the structure of $[Co(ap3d)(H_2O)](ClO_4)_2\cdot H_2O$ is given in Figure 1. Lists of the atomic coordinates of the hydrogen atoms, of the bond distances, the bond angles, and the anisotropic thermal parameters of the non-hydrogen atoms, and of the observed and calculated structure factors are available as supplementary material.

## Results and Discussion

**General Considerations.** This investigation started with the attempt to prepare *N,N,N′,N′*-tetrakis((3,5-dimethylpyrazol-1-yl)methyl)-1,3-diaminopropane (aptd). However, instead of aptd, ap3d formed. Other experiments showed that pyrazole derivatives of β-alanine, histidine, and other amino acids could not be obtained by the method described by Driessen.[1] The formation of a six-membered ring through internal hydrogen bonding may be responsible for this phenomenon. In that case one of the four hydrogen atoms is not available for condensation with *N*-(hydroxymethyl)-3,5-dimethylpyrazole. Experiments to synthesize *N,N,N′,N′*-tetrakis((pyrazol-1-yl)methyl)-1,3-diaminopropane (aptp) also failed.

Colors, X-ray diffraction types and spectroscopic information of the new ap3d compounds are given in Table IV. All compounds gave satisfactory elemental analyses.

The infrared spectra are characteristic in many details for pyrazole derivatives and for the respective anions. All spectra are very similar, and some of them are almost equal. This "infrared isomorphism" agrees with the structural isomorphism based on the X-ray powder diffraction measurements (Table IV).

**Description of the Structure of $[Co(ap3d)(H_2O)](ClO_4)_2\cdot H_2O$.** The cobalt(II) ion is surrounded by five nitrogens and one oxygen (see Figure 1). The oxygen stems from one of the two water molecules. The nitrogen atoms originate from the ligand ap3d, which utilizes in this way its maximum number of donor sites, *viz.* three pyrazole nitrogens and two amine nitrogens (one tertiary, the other secondary). The three pyrazole nitrogens and the tertiary amine lie in the equatorial plane; the secondary amine lies above this plane. The other coordination place is occupied by the water molecule, thus forming a distorted-octahedral geometry.

The coordination distances are more or less normal, the distances from the cobalt ion to the pyrazole nitrogens and the axial (secondary amine) nitrogen and the oxygen being about 2.1 Å and to the equatorial (tertiary) amine about 2.2 Å (see Table II for the exact data). The angle between the bonds of the cobalt ion to the two amines is about 93°. The N(amine)–Co–N(pyrazole) angles are about 78° and must be due to the restricted ligand bite. This observation has been reported for other amine pyrazole derivatives.[2-5]

**Table V.** ESR Parameters of the Copper ap3d Compounds and of the Copper Dopants in the Zinc ap3d Compounds at 77 K

| | $g_\parallel$ or $g_1$ | $g_2$ | $g_\perp$ | $g_3$ | $A_\parallel$, G |
|---|---|---|---|---|---|
| $[Cu(ap3d)(H_2O)](BF_4)_2$ | 2.24 | | 2.07 | | 130 |
| $[Zn(ap3d)(H_2O)](BF_4)_2$ | 2.22 | 2.06 | | 2.00 | 125 |
| $[Cu(ap3d)(H_2O)](ClO_4)_2$ | 2.22 | | 2.05 | | 165 |
| $[Zn(ap3d)(H_2O)](ClO_4)_2$ | 2.22 | 2.05 | | 2.00 | 130 |

The pyrazole rings of the ligand ap3d are planar, with normal bond lengths and angles.

The central carbon of the propane bridge shows strong thermal motion, indicating some disorder. Attempts to account for this disorder by placing the carbon atom at two different positions with fractional occupancy factors failed.

The methyl group between the secondary amine and the pyrazole ring (C30) is disordered over two different positions. Chemically these positions are equivalent.

This structure explicitly shows that the replacement of an ethylene bridge by a propylene bridge indeed is capable of forming two separate coordination places with the correct angle for an octahedral conformation. If the ligand aptd could have been formed, a (distorted) octahedral conformation indeed might have resulted.

The second water molecule is hydrogen bonded to the coordinated water molecule and also to both perchlorate ions. The coordinated water molecule forms a hydrogen bridge to one of the perchlorates. Those hydrogen bridges form a chain between the molecular entities. Because of these hydrogen bridges, the perchlorate ions show less thermal motion than expected.

**Spectroscopic Results.** To obtain further information about the coordination geometry of the metal ap3d complexes, the spectroscopic properties were investigated in some detail.

The electronic absorption spectra of the cobalt and nickel compounds reveal that these metal ions are hexacoordinated in a fashion that is close to octahedral. The ligand field parameters calculated from the positions of the absorption bands (see Table IV) are as follows: $Dq$ = 1030 cm$^{-1}$ and $B$ = 805 cm$^{-1}$ for $[Co(ap3d)(H_2O)](BF_4)_2\cdot 2H_2O$; $Dq$ = 1030 cm$^{-1}$ and $B$ = 855 cm$^{-1}$ for $[Co(ap3d)(H_2O)](ClO_4)_2\cdot H_2O$; $Dq$ = 1050 cm$^{-1}$ and $B$ = 835 cm$^{-1}$ for $[Ni(ap3d)(H_2O)](BF_4)_2\cdot 2H_2O$; and $Dq$ = 1040 cm$^{-1}$ and $B$ = 835 cm$^{-1}$ for $[Ni(ap3d)(H_2O)](ClO_4)_2$.

The broadness of the first band in the diffuse-reflectance spectra of the cobalt compounds indicates that the environment of the cobalt ions is slightly distorted-octahedral, as confirmed by the crystal structure.

The values for the spectrochemical parameters are too low for an $N_6$ chromophore; they are in better agreement with an $N_5O$ chromophore. Shapes and positions of the electronic absorption bands in the spectra of the nickel compounds reveal a slightly distorted-octahedral environment for the nickel ions. This is in agreement with the powder and IR isomorphism between the cobalt and nickel compounds. The value for the spectrochemical parameter $Dq$ is in accordance with an $N_5O$ chromophore.[9,10]

The position and shape of the absorption band in the diffuse-reflectance spectra of the copper complexes (Table IV) indicate tetragonally distorted environments of the Cu(II) ions. The two copper compounds are mutually powder and IR isomorphous, which means that the crystal packing and the molecular structure of these compounds are similar. However, the ligand field spectra and the ESR spectra (Table V) are different for these compounds, indicating that the direct copper environment in $[Cu(ap3d)(H_2O)](ClO_4)_2$ is slightly more tetragonally distorted than that in $[Cu(ap3d)(H_2O)](BF_4)_2$. This phenomenon of very slight differences in coordination geometry, responsible for relatively large spectroscopic differences, is not unusual for copper(II) compounds.[11]

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(11) Fitzgerald, W.; Hathaway, B.; Simmons, C. J. *J. Chem. Soc., Dalton Trans.* **1985**, 141.

The copper dopants in the zinc ap3d compounds show a rather large rhombic distortion, as deduced from the $g$ values of the ESR spectra. The differences observed in $A_{\parallel}$ for the Cu and Cu-doped Zn compounds must originate from small differences in coordination geometry for the $Cu^{2+}$ ions.

### Concluding Remarks

The ligand ap3d appears to be a pentadentate nitrogen donor ligand toward first-row transition-metal ions.

In all compounds studied the coordination geometry is close to octahedral, the coordination being completed by a water molecule. The constraint of the propylene bridge is much less than that of the ethylene bridge, as is deduced from the amine–Co–amine bond angle. In this way the elongation of the bridge was a successful attempt. This means that with aptd (the tetrakis(pyrazole) derivative of 1,3-diaminopropane) an octahedral coordination geometry can be expected (if the synthesis of aptd is ever successful).

Future research on ap3d and analogous ligand systems will be directed to determine which factors are responsible for the incompleteness of the amine substitution.

**Acknowledgment.** We are indebted to S. Gorter for the collection of the crystallographic data.

**Supplementary Material Available:** Listings of fractional coordinates of the hydrogen atoms, interatomic distances and bond angles and anisotropic thermal parameters of the non-hydrogen atoms, observed and calculated structure factors, and analytical data (9 pages). Ordering information is given on any current masthead page.

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(12) *Chem. Eng. News* **1983**, *61* (Dec 5), 4.

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# Redox Chemistry of Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine and Its Zinc(II) Complex in Dimethylformamide

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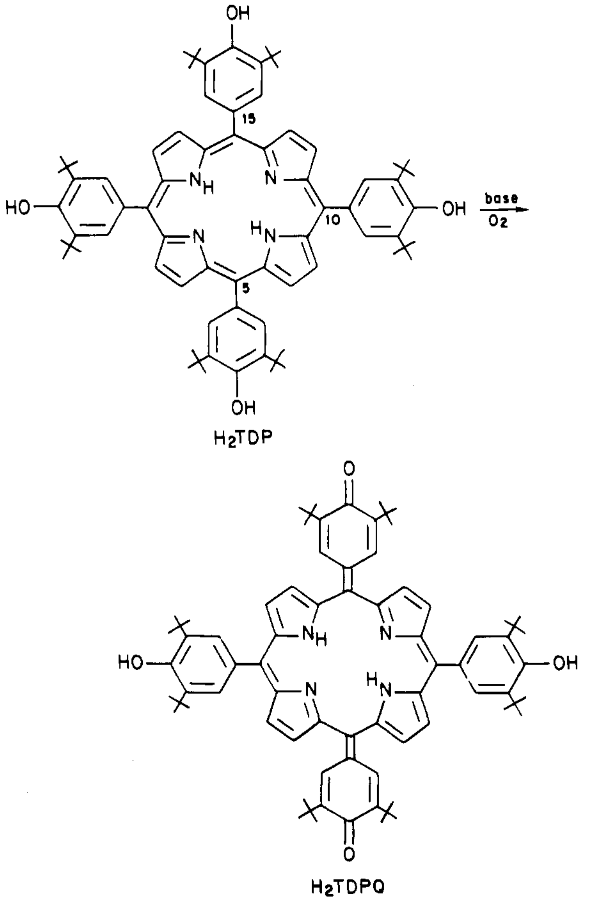
In dimethylformamide both the free ligand tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine and its zinc(II) complex exhibit electrochemistry that is characteristic of a combination of porphyrin and a hydroquinone (or catechol). Thus, the aromatic character of the tetraphenol derivative stabilizes the one-electron-oxidation products of the porphine anion and of the anion for the zinc(II) porphyrin and results in reversible electron transfer. The zinc(II)-porphyrin complex catalyzes the two-electron reduction of dioxygen.

There have been several recent reports of the chemical oxidation of tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine ($H_2TDP$) to a stable quinone-like product ($H_2TDPQ$),[1-5] similar to a 5,15-dioxoporphodimethene.[6] One example of such a reaction is its autoxidation under alkaline conditions (eq 1). Oxidation products of metalloporphyrins derived from $H_2TDP$ also have been reported, but their quinone character is less firmly established.[1-5]



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The present electrochemical and spectroscopic results provide a more complete characterization of the redox chemistry available to $H_2TDP$ and its zinc derivative, ZnTDP, as a consequence of their dual functionality: porphyrin and polyphenol. The electrochemistry of aromatic diols and quinones in aprotic media is well characterized and generally follows the sequence diol anion $\rightleftharpoons$ semiquinone anion $\rightleftharpoons$ quinone.[7] Electrochemical formation of $\pi$-cations and $\pi$-anions in porphyrins also has been studied extensively and is the subject of a recent review.[8] The goal of this study has been to determine how the well-defined redox behavior of the phenolic and porphyrin functions is manifested in $H_2TDP$ and its zinc derivative.

## Experimental Section

**Equipment.** The cyclic voltammetric (CV) and controlled-potential electrolysis (CPE) measurements were made with a three-electrode potentiostat that was equipped with a Universal programmer and digital coulometer (Princeton Applied Research Model 173-175/179). Cyclic voltammograms were recorded on a Houston Instruments Series 100 X-Y recorder.

The cell for cyclic voltammetry consisted of a Bioanalytical Systems Microcell Assembly (BAS-MF 1065) modified to accommodate a platinum-button or glassy-carbon (GCE) working electrode, a platinum-flag auxiliary electrode, and an Ag/AgCl reference electrode filled with aqueous tetramethylammonium chloride and adjusted to 0.000 V vs. SCE.[9] The reference electrode was contained in a Pyrex tube with a cracked soft-glass tip. This assembly was placed inside a Luggin capillary that contained 0.1 M electrolyte in the appropriate approtic solvent. A

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