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Supplementary Material Available: Listings of calculated and observed structure factors, thermal parameters, calculated hydrogen atom coordinates, molecular dimensions, and mean plane data and Figure 2, showing a stereoview of the unit cell contents (18 pages). Ordering information is given on any current masthead page.

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Steric Effects and the Behavior of $Cu(NN)(PPh_3)_2^+$ Systems in Fluid Solution. Crystal and Molecular Structures of $[Cu(dmp)(PPh_3)_2]NO_3$ and $[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH$

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The contrasting behavior of $Cu(phen)(PPh_3)_2^+$ and $Cu(dmp)(PPh_3)_2^+$ (phen = 1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline) in acetonitrile solution is analyzed and related to significant interligand steric repulsions that occur in the dmp complex. Both complexes undergo solvolysis with the dissociation of PPh_3, but the dissociation is more extensive for the dmp complex. At 25 °C the measured binding constants are $K^{Cu(dmp)}{}_{Cu(dmp)(L)} = 10\ (5) \times 10^4\ M^{-1}$, $K^{Cu(dmp)(L)}{}_{Cu(dmp)(L)_2} = 4\ (2) \times 10^2\ M^{-1}$, and $K^{Cu(phen)(L)}{}_{Cu(phen)(L)_2} = 2\ (1) \times 10^4\ M^{-1}$, where L stands for PPh_3. Of the various species present in solution, $Cu(dmp)(PPh_3)_2^+$ is unique in that it exhibits appreciable charge-transfer emission. Steric crowding in the coordination sphere of $Cu(dmp)(PPh_3)_2^+$ apparently inhibits solvent-induced quenching by exciplex formation, a quenching phenomenon well established in related systems. Crystal structures of the nitrate salts of each complex confirm that steric repulsions arise in the dmp complex as a result of the presence of the 2- and 9-methyl substituents. The Cu–N and Cu–P bond distances are elongated in the dmp complex relative to those in the phen derivative, and several atom–atom contacts occur at distances less than the summed van der Waals radii. For $[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH$, the crystal data are space group $P\bar{1}$, $Z = 2$, $a = 12.232\ (2)$ Å, $b = 12.496\ (2)$ Å, $c = 16.608\ (3)$ Å, $\alpha = 107.95\ (1)°$, $\beta = 90.23\ (1)°$, $\gamma = 113.62\ (1)°$, $V = 2189\ (2)$ Å^3, and $R_w = 5.3\%$ for 5805 reflections. For $[Cu(dmp)(PPh_3)_2]NO_3$, the crystal data are space group $P\bar{1}$, $Z = 2$, $a = 15.43\ (1)$ Å, $b = 13.20\ (1)$ Å, $c = 10.660\ (5)$ Å, $\alpha = 80.88\ (5)°$, $\beta = 88.98\ (4)°$, $\gamma = 94.65\ (6)°$, $V = 2136\ (2)$ Å^3, and $R_w = 6.4\%$ for 4196 reflections.

Introduction

The mixed-ligand complexes $Cu(phen)(PPh_3)_2^+$ and $Cu(dmp)(PPh_3)_2^+$, where phen and dmp denote 1,10-phenanthroline and its 2,9-dimethyl derivative, respectively, both exhibit simultaneous emissions from thermally nonequilibrated $^3\pi$–π^* and ^{3}d–π^* states in an alcohol glass.[1,2] This emissive behavior is unusual,[3] and it presumably occurs because the intraligand and charge-transfer states have different geometries and do not readily interconvert in rigid matrices.[2] The properties of the complexes are no less intriguing in fluid solution. Whereas the dmp complex is a good emitter in methanol ($\phi \approx 10^{-3}$) at room temperature, the phen complex exhibits almost no charge-transfer emission ($\phi \leqslant 10^{-5}$) under the same conditions. In the same solvent the dmp complex is prone to dissociate phosphine, while there is minimal dissociation from the phen analogue.[2]

Steric interactions are often important in complexes involving bulky phosphine ligands,[4-8] and we have suggested that steric effects could explain the differences in solution behavior of these copper systems.[2,9] In particular, steric repulsions among the 2- and 9-methyl substituents of dmp and the neighboring phosphines would promote phosphine dissociation. At the same time, steric crowding in the coordination shell would hinder the approach of a fifth ligand to the excited state. Hence solvent-induced quenching by an exciplex mechanism[9-11] would be impeded. Here we report the crystal and molecular structures of the nitrate salts of the dmp and phen complexes, and we identify the important interligand steric interactions in $Cu(dmp)(PPh_3)_2^+$. In addition, we have carried out equilibrium analyses for both complexes in acetonitrile, and we find that the ligand binding constants also reflect the steric forces.

Experimental Section

Materials and Methods. The ligands dmp (99%) and PPh_3 were purchased from Aldrich, phen was purchased from Fisher, and reagent grade $Cu(NO_3)_2{\cdot}3H_2O$ was purchased from Baker. The chemicals were of adequate purity for synthetic purposes, but the PPh_3 used in the equilibrium studies was recrystallized four times from ethanol. Yellow $[Cu(dmp)(PPh_3)_2]NO_3$ and $[Cu(phen)(PPh_3)_2]NO_3{\cdot}1^1/_2EtOH$ were prepared as reported.[2] Crystals suitable for structure determination were obtained by slow evaporation of ethanol solutions. For the absorption measurements, reagent grade acetonitrile (Mallinckrodt) sufficed; however, for the luminescence work the solvent was distilled over P_4O_{10} in order to reduce blank emission.

The absorbance measurements were taken at 25 °C for the dmp and phen complexes with copper concentrations of 1.360×10^{-4} and 1.464×10^{-4} M, respectively. Spectra were obtained as a function of added PPh_3. *Excess* PPh_3 concentrations of up to 40 times the total copper concentration were employed for the dmp complex, whereas 10 times less phosphine was used for the phen complex. The equilibrium analyses were carried out with the program SPECDEC.[12] Luminescence studies were conducted on samples of the BF_4^- salts, which had been deoxygenated

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Table I. Summary of Crystal Data and Intensity Collection

	$[Cu(phen)(PPh_3)_2]NO_3\cdot 1^1/_2EtOH$	$[Cu(dmp)(PPh_3)_2]NO_3$
fw	899.4	858.4
formula	$CuC_{51}H_{47}N_3O_{4.5}P_2$	$CuC_{50}H_{42}N_3O_3P_2$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.232 (2)	15.43 (1)
b, Å	12.496 (2)	13.20 (1)
c, Å	16.608 (3)	10.660 (5)
α, deg	107.95 (1)	80.88 (5)
β, deg	90.23 (1)	88.98 (4)
γ, deg	113.62 (1)	94.65 (6)
V, Å^3	2189 (2)	2136 (2)
Z	2	2
ρ_{calcd}, g/cm^3	1.37	1.33
$F(000)$	954	892
cryst dimens, mm	0.15 × 0.20 × 0.35	0.4 × 0.4 × 0.4
μ, cm^{-1} (Cu Kα)	18.0	16.71

by repetitive freeze/pump/thaw cycles and finally equilibrated at 25 °C in the cell holder prior to the measurement.

Apparatus. The absorption measurements were obtained with a Perkin-Elmer 320 spectrophotometer interfaced to a PE 3600 data station, which allowed for spectral digitization to ±0.001 absorbance unit. The sample cell was thermostated with a Lauda K-2/RD circulating water bath. In the luminescence work a Perkin-Elmer MPF-44B spectrofluorimeter was used. Lifetimes were determined with a N_2-pumped dye laser system as previously described.[13]

Single-crystal data for $[Cu(dmp)(PPh_3)_2]NO_3$, were collected with a Syntex P3 four-circle diffractometer and a graphite monochromator, and calculations were carried out on a CDC 6600 computer. For $[Cu(phen)(PPh_3)_2]NO_3\cdot 1^1/_2EtOH$, data collection was achieved with an Enraf-Nonius CAD4 diffractometer and all calculations were performed on a PDP-11 computer.

Structure Analysis. A block-shaped crystal of $[Cu(phen)(PPh_3)_2]NO_3\cdot 1^1/_2EtOH$ with approximate dimensions of 0.15 × 0.20 × 0.35 mm was selected for study. Preliminary examination and data collection were performed with Ni-filtered Cu Kα radiation (λ = 1.541 84 Å). The unit cell was found to be triclinic and the space group assumed to be $P\bar{1}$. (This assumption was confirmed by the structural refinement.) Cell constants (Table I) and an orientation matrix for data collection were obtained from least-squares refinement, on the basis of setting angles of 25 reflections in the range 25° < θ < 32°. The data were collected at a temperature of −140 °C with the ω–2θ scan technique with a maximum 2θ value of 120.0°. The scan rate varied from 1 to 3°/min (in ω). The scan range was corrected for the separation of the Kα doublet.[14] The ratio of peak-counting time to background-counting time was 2:1. For intense reflections an attenuator was automatically inserted in front of the detector.

A total of 6474 unique reflections were collected with $h = \pm 13$, $k = -14$ to 13, and l = 0 to 18, and 5805 reflections met the condition $F_o^2 > 2\sigma(F_o^2)$. As a check on crystal and electronic stability three representative reflections were measured every 120 min. The intensities of the standards remained constant within experimental error throughout data collection. Lorentz and polarization corrections and an empirical absorption correction based on a series of ψ scans were applied to the data. Neutral-atom scattering factors were used for all atoms.[15]

The structure was solved with SDP-PLUS,[16] and the copper position was obtained by using the Patterson heavy-atom method. The remaining atoms were located from Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The hydrogens are numbered in reference to the attached carbon. The structure was refined with a modified block-diagonal least-squares technique where the function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w was defined as $4F_o^2/\sigma^2(F_o^2)$. The final values for R and R_w were 0.041 and 0.053, respectively.

A chunky crystal of $[Cu(dmp)(PPh_3)_2]NO_3$ with an average radius of ca. 0.4 mm was characterized by rotation and Weissenberg photographs and found to be triclinic; the space group was assumed to be $P\bar{1}$. (This assumption was confirmed by the structural refinement.) Final unit cell parameters (Table I) were determined from the 2θ values of 15 reflections measured on the diffractometer with Cu Kα radiation. Intensity data were collected at 21 °C by using a θ–2θ scanning technique out to a 2θ of 116.0°. A variable scan rate was used with a maximum of 29.3°/min and a minimum of 2.02°/min. The scan range was from 1.2° less than Kα_1 to 1.2° more than Kα_2; backgrounds were counted at each end of the scan range, and the total background time was equal to that of the scan. Three standard reflections were measured every 50 reflections; the data were corrected for the 1–2% decay of the standards, assuming a linear rate of decay.

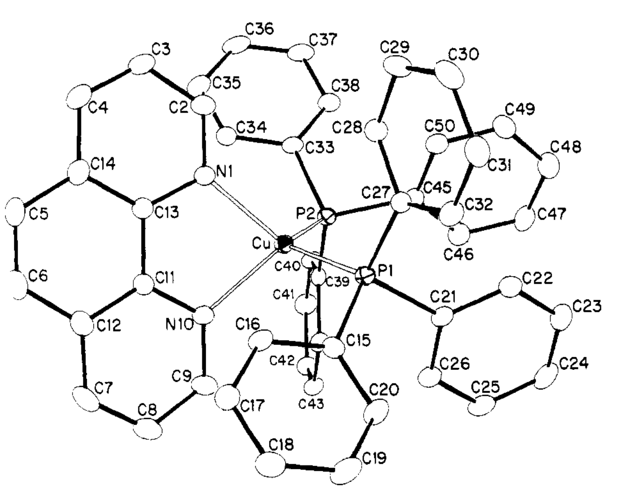

Figure 1. ORTEP diagram of the $Cu(phen)(PPh_3)_2^+$ cation showing 50% probability ellipsoids.

Of the 4450 unique reflections in a hemisphere of data with $h = \pm 9$, $k = \pm 14$, and l = 0–11, 4196 met the condition $F_o > 3\sigma(F_o)$ and were considered significant. Neutral-atom scattering factors were used for all atoms,[15] and since the crystal approximated a sphere, no absorption corrections were necessary (μR = 0.7). The structure was solved with the SHELX[17] program, and the copper position was obtained from a Patterson synthesis. The remaining non-hydrogen atoms were located by successive Fourier maps. The nitrate ion was disordered and was refined in two positions, each with an occupancy factor of $^1/_2$. The phenyl groups of the PPh_3 ligands were refined as rigid bodies. Hydrogen atom positions were calculated in order to elucidate the steric interactions, but they were not refined nor were they included in structure factor calculations. Each hydrogen was numbered like the carbon it was bonded to. All non-hydrogen atoms were refined with anisotropic parameters. The structure was refined with a modified block-diagonal least-squares technique where $\sum w(|F_o| - |F_c|)^2$ was minimized, and the weight w was defined as $4F_o^2/\sigma^2(F_o^2)$. The final R and R_w values were both 0.064.

Positional coordinates for the non-hydrogen atoms in $[Cu(phen)(PPh_3)_2]NO_3\cdot 1^1/_2EtOH$ and $[Cu(dmp)(PPh_3)_2]NO_3$ are listed in Tables II and III, respectively. Selected bond distances and bond angles are given in Table IV. Tables containing additional distances and angles, the calculated positions of the hydrogen atoms, the anisotropic thermal parameters, relevant least-squares planes, and structure factors (Tables VI–XIV) are available as supplementary material.

Results and Discussion

Structure of $[Cu(phen)(PPh_3)_2]NO_3\cdot 1^1/_2EtOH$. The ORTEP diagram of the cation along with the atom-numbering scheme is illustrated in Figure 1. The structure consists of discrete $Cu(phen)(PPh_3)_2^+$ and NO_3^- ions, with the ethanol molecules hydrogen-bonded to the anion. The coordination geometry about Cu(I) can be described as distorted tetrahedral with an N_2P_2 donor set. The average Cu–N and Cu–P distances are 2.075 (2) and 2.258 (1) Å, respectively. The Cu–N distance is comparable to those of $Cu(dmp)_2^+$ (2.054 (7) Å)[18-22] and $Cu(bpy)(PPh_3)Cl$

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Table II. Final Positional Parameters of Non-Hydrogen Atoms of [Cu(phen)(PPh$_3$)$_2$]NO$_3$·1^1/$_2$EtOH

atom	*x*	*y*	*z*
Cu	0.22261 (3)	0.50129 (3)	0.30052 (2)
P1	0.34920 (6)	0.40646 (6)	0.27136 (4)
P2	0.12841 (6)	0.50592 (6)	0.18617 (4)
O1	0.0651 (2)	0.9533 (2)	0.7777 (2)
O2	0.1598 (3)	0.9850 (2)	0.6710 (2)
O3	0.2584 (2)	1.0501 (2)	0.7955 (2)
NO3	0.1582 (2)	0.9966 (2)	0.7472 (2)
N1	0.2818 (2)	0.6714 (2)	0.3975 (1)
C2	0.3402 (2)	0.7858 (3)	0.3944 (2)
C3	0.3637 (3)	0.8925 (3)	0.4644 (2)
C4	0.3334 (3)	0.8822 (3)	0.5421 (2)
C5	0.2393 (3)	0.7420 (3)	0.6266 (2)
C6	0.1773 (3)	0.6257 (3)	0.6276 (2)
C7	0.0716 (3)	0.3973 (3)	0.5482 (2)
C8	0.0365 (3)	0.3021 (3)	0.4715 (2)
C9	0.0704 (2)	0.3283 (3)	0.3973 (2)
N10	0.1368 (2)	0.4425 (2)	0.3970 (1)
C11	0.1729 (2)	0.5371 (3)	0.4735 (2)
C12	0.1410 (2)	0.5196 (3)	0.5512 (2)
C13	0.2455 (2)	0.6608 (2)	0.4732 (2)
C14	0.2737 (2)	0.7630 (3)	0.5485 (2)
C15	0.3589 (2)	0.3289 (3)	0.3469 (2)
C16	0.3663 (2)	0.3915 (2)	0.4332 (2)
C17	0.3709 (3)	0.3382 (3)	0.4947 (2)
C18	0.3674 (3)	0.2205 (3)	0.4694 (2)
C19	0.3606 (4)	0.1573 (3)	0.3837 (2)
C20	0.3562 (3)	0.2105 (3)	0.3224 (2)
C21	0.3008 (2)	0.2820 (2)	0.1682 (2)
C22	0.3651 (3)	0.2843 (3)	0.0993 (2)
C23	0.3158 (3)	0.1909 (3)	0.0204 (2)
C24	0.2035 (3)	0.0947 (3)	0.0100 (2)
C25	0.1396 (3)	0.0901 (3)	0.0782 (2)
C26	0.1878 (3)	0.1842 (3)	0.1572 (2)
C27	0.5066 (2)	0.5055 (2)	0.2719 (2)
C28	0.5383 (3)	0.6309 (3)	0.2845 (2)
C29	0.6582 (3)	0.7128 (3)	0.2908 (2)
C30	0.7465 (3)	0.6691 (3)	0.2830 (2)
C31	0.7160 (3)	0.5447 (3)	0.2697 (2)
C32	0.5973 (3)	0.4637 (3)	0.2648 (2)
C33	0.1246 (2)	0.6545 (2)	0.1949 (2)
C34	0.1012 (2)	0.7208 (3)	0.2719 (2)
C35	0.0914 (3)	0.8305 (3)	0.2814 (2)
C36	0.1057 (3)	0.8766 (3)	0.2139 (2)
C37	0.1308 (3)	0.8124 (3)	0.1373 (2)
C38	0.1397 (2)	0.7014 (3)	0.1279 (2)
C39	−0.0304 (2)	0.3964 (2)	0.1527 (2)
C40	−0.1147 (3)	0.4221 (3)	0.1145 (2)
C41	−0.2339 (3)	0.3364 (3)	0.0914 (2)
C42	−0.2709 (3)	0.2240 (3)	0.1049 (2)
C43	−0.1884 (3)	0.1971 (3)	0.1422 (2)
C44	−0.0690 (3)	0.2829 (3)	0.1661 (2)
C45	0.2001 (2)	0.4742 (3)	0.0907 (2)
C46	0.1416 (3)	0.3721 (3)	0.0166 (2)
C47	0.2015 (3)	0.3524 (3)	−0.0533 (2)
C48	0.3200 (3)	0.4348 (3)	−0.0505 (2)
C49	0.3783 (3)	0.5364 (3)	0.0237 (2)
C50	0.3196 (3)	0.5557 (3)	0.0935 (2)
O4	0.4919 (2)	0.1264 (2)	0.7525 (1)
C51	0.5385 (3)	0.0538 (3)	0.7806 (2)
C52	0.5408 (3)	0.0759 (3)	0.8753 (2)
O5[a]	0.1358 (5)	0.9812 (5)	0.5069 (4)
C60	0.0651 (4)	1.0392 (4)	0.4999 (3)

[a] Half-occupancy.

Table III. Final Positional Parameters for Non-Hydrogen Atoms of [Cu(dmp)(PPh$_3$)$_2$]NO$_3$

atom	*x*	*y*	*z*
N1	0.1551 (4)	0.2597 (4)	0.3734 (5)
C2	0.1004 (5)	0.1730 (6)	0.3887 (8)
C3	0.0364 (6)	0.1569 (8)	0.2980 (10)
C4	0.0270 (6)	0.2327 (10)	0.1934 (10)
C5	0.0752 (7)	0.4091 (10)	0.0728 (8)
C6	0.1268 (7)	0.4973 (9)	0.0653 (8)
C7	0.2456 (7)	0.6028 (7)	0.1557 (9)
C8	0.3051 (6)	0.6094 (6)	0.2473 (9)
C9	0.3133 (5)	0.5244 (5)	0.3450 (7)
N10	0.2648 (4)	0.4348 (4)	0.3478 (5)
C11	0.1467 (5)	0.3345 (6)	0.2698 (6)
C12	0.0829 (6)	0.3245 (8)	0.1781 (7)
C13	0.2031 (5)	0.4281 (5)	0.2587 (6)
C14	0.1926 (6)	0.5103 (7)	0.1585 (6)
C15	0.1072 (6)	0.0956 (6)	0.5070 (8)
C16	0.3764 (5)	0.5359 (5)	0.4496 (7)
Cu17	0.2615 (1)	0.2972 (1)	0.4832 (1)
P18	0.2162 (1)	0.3394 (1)	0.6740 (1)
P19	0.3651 (1)	0.1853 (1)	0.4688 (1)
C20	0.1799 (3)	0.4699 (2)	0.6464 (4)
C21	0.1296 (3)	0.4953 (2)	0.5404 (4)
C22	0.0993 (3)	0.5929 (2)	0.5140 (4)
C23	0.1192 (3)	0.6651 (2)	0.5937 (4)
C24	0.1696 (3)	0.6398 (2)	0.6998 (4)
C25	0.1999 (3)	0.5423 (2)	0.7261 (4)
C26	0.1201 (3)	0.2640 (3)	0.7582 (4)
C27	0.0399 (3)	0.3049 (3)	0.7638 (4)
C28	−0.0326 (3)	0.2429 (3)	0.8193 (4)
C29	−0.0248 (3)	0.1398 (3)	0.8693 (4)
C30	0.0555 (3)	0.0990 (3)	0.8637 (4)
C31	0.1279 (3)	0.1610 (3)	0.8081 (4)
C32	0.2965 (3)	0.3417 (3)	0.7989 (4)
C33	0.2716 (3)	0.3319 (3)	0.9270 (4)
C34	0.3345 (3)	0.3373 (3)	1.0185 (4)
C35	0.4224 (3)	0.3527 (3)	0.9819 (4)
C36	0.4475 (3)	0.3626 (3)	0.8538 (4)
C37	0.3845 (3)	0.3570 (3)	0.7623 (4)
C38	0.4178 (3)	0.1448 (3)	0.6209 (3)
C39	0.3635 (3)	0.1079 (3)	0.7271 (3)
C40	0.3990 (3)	0.0857 (3)	0.8469 (3)
C41	0.4887 (3)	0.1005 (3)	0.8603 (3)
C42	0.5429 (3)	0.1375 (3)	0.7540 (3)
C43	0.5074 (3)	0.1596 (3)	0.6344 (3)
C44	0.3176 (3)	0.0661 (3)	0.4202 (4)
C45	0.3107 (3)	−0.0285 (3)	0.5009 (4)
C46	0.2689 (3)	−0.1150 (3)	0.4608 (4)
C47	0.2342 (3)	−0.1069 (3)	0.3401 (4)
C48	0.2412 (3)	−0.0123 (3)	0.2594 (4)
C49	0.2828 (3)	0.0742 (3)	0.2994 (4)
C50	0.4576 (2)	0.2218 (3)	0.3545 (4)
C51	0.4905 (2)	0.3249 (3)	0.3307 (4)
C52	0.5646 (2)	0.3545 (3)	0.2526 (4)
C53	0.6059 (2)	0.2810 (3)	0.1984 (4)
C54	0.5731 (2)	0.1780 (3)	0.2222 (4)
C55	0.4989 (2)	0.1484 (3)	0.3003 (4)
O56	0.8210 (5)	0.2221 (5)	0.0695 (6)
N57[a]	0.779 (2)	0.1462 (8)	0.053 (3)
O58[a]	0.779 (1)	0.0637 (7)	0.098 (2)
O59[a]	0.719 (1)	0.153 (1)	0.015 (2)
O60[a]	0.811 (2)	0.095 (1)	0.208 (2)
N61[a]	0.799 (2)	0.134 (1)	0.102 (2)
O62[a]	0.769 (2)	0.083 (1)	0.029 (2)

[a] Half-occupancy.

(2.081 (5) Å)[23] as well as [Cu(bpy)(PPh$_3$)$_2$]ClO$_4$ (2.085 (9) Å).[24] The average Cu–P distance is also similar to those of the bis(phosphine) complexes of Cu(I) discussed by Lippard and Palenik[5] and White.[24] The P–Cu–P angle in Cu(phen)(PPh$_3$)$_2^+$ is 115.44 (4)°. It is comparable to the angle observed in [Cu(PPh$_3$)$_2$(py)$_2$]ClO$_4$ (115.85 (9)°),[24] but significantly smaller than for other pseudotetrahedral bis(phosphine) molecules where the remaining two coordination sites are occupied by a bidentate ligand.[24,25] The Cu–P distance and the P–Cu–P angle do not follow the empirical

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Table IV. Selected Interatomic Distances (Å) and Bond Angles (deg)

$[Cu(phen)(PPh_3)_2]NO_3 \cdot 1^1/_2EtOH$		$[Cu(dmp)(PPh_3)_2]NO_3$	
Distances			
Cu-P1	2.271 (1)	Cu-P18	2.305 (2)
Cu-P2	2.245 (1)	Cu-P19	2.282 (2)
Cu-N1	2.070 (2)	Cu-N1	2.105 (6)
Cu-N10	2.080 (2)	Cu-N10	2.129 (4)
P1-C15	1.835 (4)	C20-P18	1.836 (4)
P1-C21	1.821 (2)	C26-P18	1.850 (5)
P1-C27	1.823 (3)	C32-P18	1.838 (5)
P2-C33	1.837 (3)	C38-P19	1.848 (4)
P2-C39	1.830 (2)	C44-P19	1.835 (4)
P2-C45	1.828 (3)	C50-P19	1.842 (4)
N1-C2	1.335 (4)	C2-N1	1.352 (9)
N1-C13	1.364 (4)	C2-C3	1.422 (13)
C2-C3	1.395 (4)	C2-C15	1.503 (11)
C3-C4	1.374 (5)	C3-C4	1.393 (14)
C4-C14	1.410 (4)	C4-C12	1.415 (15)
C5-C6	1.348 (5)	C5-C6	1.347 (17)
C5-C14	1.434 (4)	C5-C12	1.466 (13)
C6-C12	1.433 (4)	C6-C14	1.453 (13)
C7-C8	1.369 (4)	C7-C8	1.361 (14)
C7-C12	1.404 (4)	C7-C14	1.409 (12)
C8-C9	1.394 (5)	C8-C9	1.419 (10)
C9-N10	1.331 (4)	C9-N10	1.344 (8)
N10-C11	1.364 (3)	C9-C16	1.511 (11)
C11-C12	1.404 (4)	C11-N1	1.375 (8)
C11-C13	1.443 (4)	C11-C12	1.413 (11)
C13-C14	1.405 (3)	C11-C13	1.440 (10)
		C13-C14	1.418 (10)
		C13-N10	1.365 (9)
Angles			
P1-Cu-P2	115.44 (4)	P18-Cu-P19	122.7 (1)
P1-Cu-N1	118.69 (7)	N1-Cu-P18	111.4 (2)
P1-Cu-N10	103.60 (8)	N10-Cu-P18	106.4 (2)
P2-Cu-N1	109.82 (8)	N1-Cu-P19	109.4 (2)
P2-Cu-N10	124.55 (7)	N10-Cu-P19	119.0 (2)
N1-Cu-N10	80.90 (9)	N1-Cu-N10	80.1 (2)

correlation of Lippard and Palenik.[5]

The phen ligand is slightly buckled. The coordinating nitrogens, N1 and N10, are positioned below (0.145 Å) and above (0.057 Å) the least-squares plane, respectively. The dihedral angle between the plane of the phen ligand and the plane defined by the Cu and the two phosphorus atoms is 73.35°. Two ethanol molecules are within hydrogen-bonding distance of the NO_3^- anion. The hydrogen bond contacts are 2.722 (7) Å between O2 and O5 and 2.798 (4) Å between O3 and O4. One of the ethanol molecules is subject to a 2-fold disorder about a center of symmetry.

Structure of $[Cu(dmp)(PPh_3)_2]NO_3$. There are no unusually short cation–anion distances in the structure, and the nitrate anion is disordered over two positions. Figure 2 illustrates the atom-numbering scheme in the cation. The coordination geometry about Cu(I) is also distorted tetrahedral with average Cu–N and Cu–P distances of 2.117 (5) Å and 2.293 (2) Å, respectively. By comparison to $Cu(phen)(PPh_3)_2^+$, the copper-to-ligand distances are increased. The P–Cu–P angle in $Cu(dmp)(PPh_3)_2^+$ is 122.7 (1)°. In keeping with the rigidity of the dmp framework and the longer Cu–N bonds, the N–Cu–N bite angle is about 2° smaller in this structure than in $Cu(dmp)_2^+$ and about 1° smaller than in $Cu(phen)(PPh_3)_2^+$. The dmp moiety is slightly "bowed" with the bay atoms (N1, C11, C13, and N10) displaced above the least-squares plane through the ligand. Except for C9 and C12, all other carbons of the dmp ligand are found below the plane. The copper atom is displaced 0.235 Å above the dmp plane, and the dihedral angle between this plane and the plane defined by Cu and the two phosphorus atoms is 82.2°. The bond angles and bond distances within the nitrate counterion are equivalent in both orientations. The position of one of the oxygen atoms (O56) is common to both sites, and the sites differ by about 30° in the relative orientation of the bond vector between this oxygen and the nitrate nitrogen.

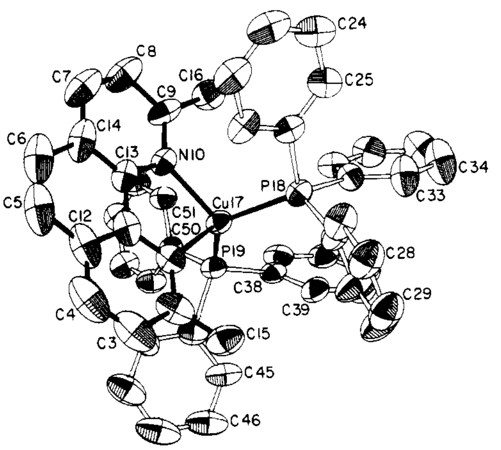

Figure 2. ORTEP diagram of the $Cu(dmp)(PPh_3)_2^+$ cation showing 50% probability ellipsoids. The carbons are numbered consecutively about each phenyl ring of the PPh_3 groups. The carbons connected to P19 are C38, C44, and C50. Those connected to P18 are C20, C26, and C32.

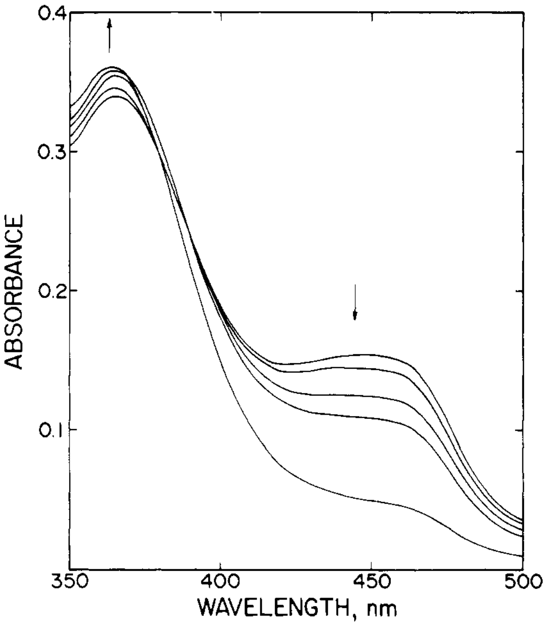

Figure 3. Absorption spectra of $Cu(dmp)(PPh_3)_2^+$ solutions in acetonitrile at 25 °C. The copper concentration was 1.360×10^{-4} M. The arrows indicate the direction of the absorbance change as increasing amounts of PPh_3 were added. Excess PPh_3 concentrations were 0, 0.114×10^{-3}, 0.560×10^{-3}, 1.134×10^{-3}, and 5.672×10^{-3} M.

Equilibrium Studies. The absorption spectra of a series of acetonitrile solutions containing $Cu(dmp)(PPh_3)_2^+$ are presented in Figure 3. An increase in the absorption maximum at 365 nm, and a decrease in a shoulder at 450 nm is observed upon the addition of PPh_3. Analogous spectral changes were previously observed in methanol and were ascribed to

$$Cu(dmp)(PPh_3)_2^+ \rightleftharpoons Cu(dmp)^+ + 2PPh_3 \qquad (1)$$

while the absorbance at 450 nm was attributed to $Cu(dmp)^+$.[2] However, attempts to fit the data resulted in calculated absorbances that are well outside experimental error. A more elaborate model is described by the following equations:

$$Cu^+ + nPPh_3 \rightleftharpoons Cu(PPh_3)_n^+ \qquad (2)$$

$$Cu^+ + dmp \rightleftharpoons Cu(dmp)^+ \qquad (3)$$

$$Cu(dmp)^+ + dmp \rightleftharpoons Cu(dmp)_2^+ \qquad (4)$$

$$Cu(dmp)^+ + PPh_3 \rightleftharpoons Cu(dmp)(PPh_3)^+ \qquad (5)$$

$$Cu(dmp)(PPh_3)^+ + PPh_3 \rightleftharpoons Cu(dmp)(PPh_3)_2^+ \qquad (6)$$

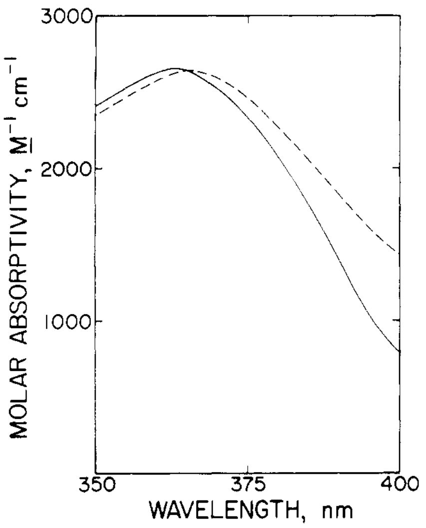

Figure 4. Resolved absorption spectra of $Cu(dmp)(PPh_3)_2^+$ (—) and $Cu(dmp)(PPh_3)^+$ (---) in acetonitrile at 25 °C. The estimated error in ϵ at any given wavelength is 5%.

Cu(I) is assumed to be four-coordinate throughout, although for ease of notation, coordinated solvent molecules are not specified. In addition, the anion is assumed to be uncoordinated. To facilitate the analysis, we have characterized the equilibria in acetonitrile since in this medium $K^{Cu}{}_{Cu(dmp)} = 1 \times 10^6$ M^{-1} and $K^{Cu(dmp)}{}_{Cu(dmp)_2} = 8 \times 10^4$ M^{-1} and the molar absorptivities of $Cu(dmp)^+$ and $Cu(dmp)_2^+$ are known.[12]

In the initial analysis, eq 2 and the associated $K^{Cu}{}_{Cu(L)_n}$ values, where L denotes PPh_3, were ignored. This was possible because the absorbance data are only indirectly related to the $Cu(PPh_3)_n^+$ species, and they were expected to be minor species. Estimates for $K^{Cu(dmp)}{}_{Cu(dmp)(L)}$ and $K^{Cu(dmp)(L)}{}_{Cu(dmp)(L)_2}$ were obtained from a series of maps of the error surface and then further refined with SPECDEC. In addition, a small correction was made for the absorbance of the free phosphine, which was always present in excess. The best fit of the data occurred with $K^{Cu(dmp)}{}_{Cu(dmp)(L)} = 10\ (5) \times 10^4$ M^{-1} and $K^{Cu(dmp)(L)}{}_{Cu(dmp)(L)_2} = 4\ (2) \times 10^2$ M^{-1}. The standard deviation between the calculated and measured absorbances was quite satisfactory ($\sigma = 1.5 \times 10^{-3}$). Inclusion of $Cu(PPh_3)^+$ gave no significant improvement in the fit, and $K^{Cu}{}_{Cu(L)}$ was estimated to be less than or equal to 10 M^{-1}. Therefore, eq 2 was dropped from the model. Resolved spectra for $Cu(dmp)(PPh_3)^+$ and $Cu(dmp)(PPh_3)_2^+$ are presented in Figure 4.

Absorption spectra for solutions containing $Cu(phen)(PPh_3)_2^+$ and varying amounts of PPh_3 are presented in Figure 5. There is no evidence of a shoulder at 440 nm, a characteristic absorption wavelength of $Cu(phen)_2^+$, and only 4 equiv of excess PPh_3 are necessary to reach a limiting absorbance at 365 nm. Dissociation of phosphine is clearly less extensive for this complex, and an excellent fit of the absorbance data ($\sigma = 7.5 \times 10^{-4}$) can be obtained with the assumption that

$$Cu(phen)(PPh_3)^+ + PPh_3 \rightleftharpoons Cu(phen)(PPh_3)_2^+ \qquad (7)$$

is the only important equilibrium process. With a procedure analogous to the one used above, the formation constant is estimated to be $K^{Cu(phen)(L)}{}_{Cu(phen)(L)_2} = 2\ (1) \times 10^4$ M^{-1}. The analysis predicts that the absorption maximum of $Cu(phen)(PPh_3)^+$ occurs at 360 nm with $\epsilon = 2200 \pm 100$ M^{-1} cm^{-1} while the corresponding peak in the spectrum of $Cu(phen)(PPh_3)_2^+$ occurs at 366 nm with $\epsilon = 2800 \pm 100$ M^{-1} cm^{-1}.

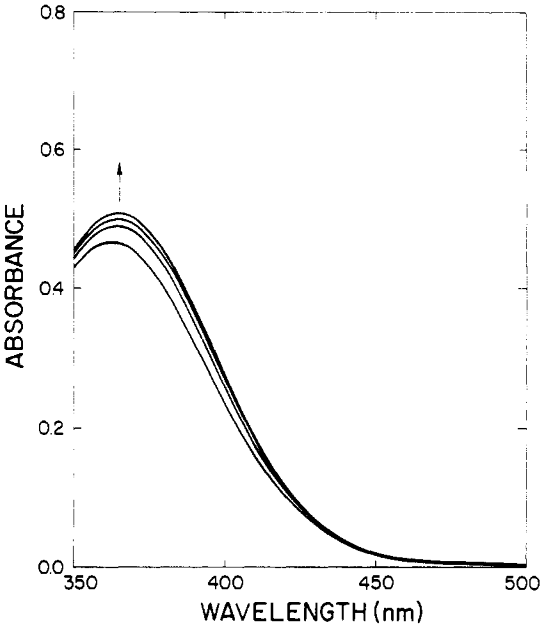

Figure 5. Absorption spectra of $Cu(phen)(PPh_3)_2^+$ solutions in acetonitrile at 25 °C. The copper concentration was 1.464×10^{-4} M. The arrow indicates the direction of the absorbance change as increasing amounts of PPh_3 were added. Excess PPh_3 concentrations were 0, 0.155×10^{-3}, 0.310×10^{-3}, 0.465×10^{-3}, and 0.620×10^{-3} M. In the region shown, the spectra of the two solutions with the highest concentrations of excess PPh_3 are indistinguishable.

Table V. Through-Space Contacts in $[Cu(dmp)(PPh_3)_2]^+$

methyl group–atom	dist, Å	summed van der Waals radii,[a] Å
Methyl Contacts with P19 Ligand		
C15–C44	3.43	3.85
C15–C45	3.66	3.85
C15–C48	3.83	3.85
C15–C49	3.52	3.85
C16–H51	2.71	3.20
C16–C51	3.78	3.85
Methyl Contacts with P18 Ligand		
C15–C26	3.73	3.85
C15–C31	3.47	3.85
C16–H37	3.01	3.20
C16–C37	3.78	3.85
C16–C20	3.63	3.85

[a] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 120.

PPh_3 Binding Constants. The modest equilibrium constants of 10^2–10^5 M^{-1} for the binding of PPh_3 (<10 M^{-1} for Cu^+) reflect the competitive binding of the solvent acetonitrile, a good ligand for Cu(I).[26] We find that even with a 40-fold excess of PPh_3 (solution 5, Figure 3), only about 53% of the total copper exists as $Cu(dmp)(PPh_3)_2^+$ in acetonitrile. In contrast a 10-fold excess of PPh_3 was sufficient to drive the formation of $Cu(dmp)(PPh_3)_2^+$ essentially to completion in methanol.[2] The fact that $Cu(dmp)^+$ has a much higher affinity for PPh_3 than Cu^+ is probably a synergic effect associated with a good σ donor like PPh_3 in company with the π-acid dmp.[27] Addition of a second PPh_3 to $Cu(dmp)(PPh_3)^+$ is much less favorable (eq 5 vs. eq 6). In contrast, $Cu(phen)(PPh_3)^+$ shows a high affinity for the second phosphine. The difference in behavior can be attributed to steric effects that are present in $Cu(dmp)(PPh_3)_2^+$.

The steric crowding within $Cu(dmp)(PPh_3)_2^+$ is manifested in its structure by relatively long copper-to-nitrogen and copper-to-phosphorus bond distances (compared with those of $Cu(phen)(PPh_3)_2^+$) and by close contacts between the methyl substituents of the dmp ligand and peripheral atoms of the phosphine ligands (Table V). In $Cu(phen)(PPh_3)_2^+$ there appear to be only minor contacts between atoms on different ligands. Possible interactions are C2–H28 (2.95 Å), C2–H34 (2.90 Å), and C11–H16 (2.80 Å) where the van der Waals distance between

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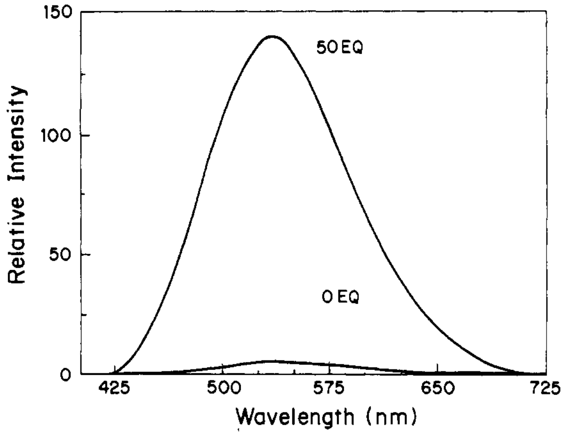

Figure 6. Uncorrected emission of $Cu(dmp)(PPh_3)_2^+$ in acetonitrile at 25 °C as a function of added PPh_3. The copper concentration was 1.362×10^{-4} M, and the excess PPh_3 concentrations were 6.752×10^{-3} and 0 M.

a hydrogen atom and an aryl carbon atom should be about 3.05 Å. Neither complex has any crystallographically required symmetry, and as one would expect, the Cu–N bonds, Cu–P bonds, etc., are inequivalent. Although a number of factors, including packing forces, may be important in determining geometry, it does seem likely that the proposed steric interactions also explain the course of particular low-symmetry distortions in $Cu(dmp)(PPh_3)_2^+$. For example, in this complex the dmp ligand is bowed and the C15 methyl group is displaced 0.12 Å out of the least-squares plane of the ligand atoms. This dislocation is probably due to the fact that the C15 methyl impinges upon the face of the phenyl group that is associated with P19 and which contains C44, C45, C48 and C49. A similar interaction, although not as severe, occurs with C26 and C31 from the other phosphine ligand. The C16 methyl experiences quite different steric repulsions, the most severe of which may involve contact with H51. This interaction is an apparent one since the hydrogen atoms of the phosphine were not refined. However, the interaction is predicted to occur largely within the plane of the ligand, and in line with the analysis, we find a longer Cu–N bond distance and a wider nitrogen–carbon–methyl angle on the C16 side of the dmp ligand. In addition, the C16 methyl group is much less removed from the ligand plane than the C15 methyl group (0.04 vs. 0.12 Å).

Luminescence Behavior. The same steric effects that are responsible for the tendency of $Cu(dmp)(PPh_3)_2^+$ to dissociate also account for the disparate emissive properties of $Cu(dmp)(PPh_3)_2^+$ and $Cu(phen)(PPh_3)_2^+$. Whereas both complexes emit well in the solid state,[28] the emission from the phen complex is almost completely quenched in donor solvents.[2] Similar quenching effects have been observed in related copper systems and have been attributed to exciplex interactions involving an increase in the coordination number at the metal.[9-11] Although the exciplex geometry would differ from that of the ground state, steric problems are expected to be even worse in a 5-coordinate structure. Thus the steric congestion inherent in $Cu(dmp)(PPh_3)_2^+$ would be expected to inhibit exciplex formation and to suppress solvent-induced quenching. On the other hand, the replacement of a bulky phosphine with a solvent molecule would relieve the steric crowding and promote exciplex formation. Consistent with this reasoning, efficient charge-transfer emission is only observed from acetonitrile solutions of $[Cu(dmp)(PPh_3)_2]BF_4$ when a large excess of PPh_3 is present (see Figure 6), and $Cu(dmp)(PPh_3)_2^+$ is the major species in solution. In the absence of excess PPh_3, when $Cu(dmp)(PPh_3)^+$ is the predominant copper-containing species, little emission can be detected.

Conclusions

The crystal and molecular structures of $[Cu(dmp)(PPh_3)_2]NO_3$ and $[Cu(phen)(PPh_3)_2]NO_3 \cdot 1^1/_2EtOH$ have been solved. A comparison of the two structures reveals that significant interligand steric repulsions are present in the dmp complex due to the interaction of the 2- and 9-methyl substituents with the peripheral atoms of PPh_3. This favors the solvolysis of one PPh_3 to yield $Cu(dmp)(PPh_3)^+$, the predominant species in acetonitrile solution with no excess PPh_3. Solvolysis of PPh_3 occurs with both complexes, and the relative magnitudes of the stability constants are consistent with the observed steric effects. Although steric effects cause problems in defining speciation in the ground state, solvent-induced quenching of the excited state via exciplex formation is inhibited when there is crowding in the coordination sphere about copper. As a result, in donor solvents the quantum yield for emission from $Cu(dmp)(PPh_3)_2^+$ is much greater than that from $Cu(phen)(PPh_3)_2^+$.

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Registry No. $[Cu(phen)(PPh_3)_2]NO_3 \cdot 1^1/_2EtOH$, 98587-01-0; $[Cu(dmp)(PPh_3)_2]NO_3$, 98587-02-1; $[Cu(phen)(PPh_3)_2]^+$, 47886-23-7; $[Cu(dmp)(PPh_3)_2]^+$, 78809-58-2.

Supplementary Material Available: Tables containing additional bond distances and angles, hydrogen coordinates, thermal parameters, least-squares planes, and observed and calculated structure amplitudes (66 pages). Ordering information is given on any current masthead page.

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