Synthesis, Spectroscopy, and Electrochemistry of Trinuclear Copper(I) Acetylides. X-ray Crystal Structure of $[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)]PF_6$

Vivian Wing-Wah Yam,* Wai-Kit Lee, and Ting-Fong Lai[†]

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Received November 10, 1992

Summary: The synthesis, characterization, and X-ray crystal structure of $[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)]PF_6$ (3) are described; complex 3 and two other trinuclear copper(I) acetylide complexes are shown to exhibit long-lived photoluminescence at room temperature.

Introduction

There has been growing interest in the synthesis of alkynylmetal complexes owing to the recent reports on their potential applications as nonlinear optical materials.[1] The wide and selective applications of alkynylcopper(I) complexes in organic chemistry have also attracted much attention. However, their chemistry has not been as extensively studied as the aryl and alkyl counterparts owing to their insolubility in common solvents, which precludes in many cases structural characterization studies. Moreover, despite the rich photophysical and photochemical behavior exhibited by a wide variety of polynuclear d^{10} metal complexes,[2-4] there has been no report of detailed photophysical studies of alkynylcopper(I) clusters.

We report here the first example of trinuclear copper(I) acetylides that exhibit luminescence at room temperature both in the solid state and in fluid solutions.

Experimental Section

Materials and Reagents. The ligand bis(diphenylphosphino)methane (dppm) was obtained from Strem Chemicals, Inc. $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ was prepared by a literature procedure.[5] Phenylacetylene and 3,3-dimethylbut-1-yne were obtained from Aldrich Chemical Co. All solvents were purified and distilled using standard procedures before use.[6] All other reagents were of analytical grade and were used as received.

Syntheses of Copper Complexes. All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2]PF_6$ (1). This was prepared by the method described in the literature.[7] UV/vis (MeCN), λ/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 255 (sh) (48 825), 305 sh (32 390).

$[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2]PF_6$ (2). A solution of the complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ (127 mg, 0.10 mmol) in THF/MeOH (v/v 3:1; 12 mL) was treated with 3,3-dimethylbut-1-yne (16.2 μL, 0.13 mmol) and an excess of KOH and stirred at room temperature for 24 h. After evaporation to dryness, the resulting solid was extracted with THF (3 × 8 mL), and the solution was filtered and reduced in volume. Subsequent diffusion of diethyl ether into the concentrated solution gave 2 as air-stable colorless crystals (yield 67 mg, 40%). UV/vis (MeCN), λ/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 255 (sh) (39 280), 350 (sh) (6150). ^{1}H NMR (CD_3CN, δ ppm): δ 1.46 (s, 18H, ^{t}Bu), 3.15 (m, 6H, $-CH_2-$), 6.87-7.21 (m, 60H, Ph-). Anal. Calcd for $C_{87}H_{84}P_7F_6Cu_3\cdot H_2O$: C, 62.60; H, 5.20. Found: C, 62.58; H, 5.05.

$[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)]PF_6$ (3). The procedure is similar to that described for the preparation of 1 except 3,3-dimethylbut-1-yne was used in place of phenylacetylene. Air-stable pale yellow crystals of 3 could be obtained by slow diffusion of diethyl ether vapor into a dichloromethane solution of the salt. Yield: 73 mg (45%). UV/vis (MeCN), λ/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 255 (sh) (42 170), 330 (sh) (6950). Anal. Calcd for $C_{81}H_{75}P_7ClF_6Cu_3$: C, 60.57; H, 4.71; Cl, 2.21. Found: C, 60.32; H, 4.51; Cl, 2.25.

Physical Measurements and Instrumentation. UV-visible spectra were obtained on a Milton Roy Spectronic 3000 diode array spectrophotometer, IR spectra were obtained as Nujol mulls on a Shimadzu IR-470 infrared spectrophotometer (4000-400 cm^{-1}), and steady-state excitation and emission spectra were obtained on a Spex Fluorolog 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded from 4:1 ethanol-methanol glass matrices by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer with chemical shifts reported relative to TMS. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G-resonator). Luminescence decay signals were recorded on a Tektronix Model 2430 digital oscilloscope and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under

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[†] To whom X-ray correspondence should be addressed.

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Table I. Crystal and Structure Determination Data for 3

formula	$Cu_3C_{81}H_{75}P_6Cl{\cdot}PF_6$
fw	1605.37
T, °C	22
a, Å	10.559(3)
b, Å	27.602(7)
c, Å	25.855(6)
β, deg	94.10(2)
V, Å^3	7516(6)
cryst syst	monoclinic
space group	$P2_1/c$
Z	4
$F(000)$	3296
ρ_{calcd}, g cm^{-3}	1.419
cryst color/shape	colorless prism
cryst dimens, mm	0.18 × 0.21 × 0.25
λ, Å (graphite monochromated, Mo Kα)	0.710 73
μ, cm^{-1}	10.8
transm factors	0.968–0.999
collcn range	$2\theta_{max} = 50°$; $(h,k,\pm l)$
scan mode and scan speed, deg min^{-1}	ω–2θ; 0.97–5.49
scan width, deg	$0.60 + 0.34 \tan \theta$
bckgd time	0.5 × scan time
no. of data collcd	14 308
no. of unique data	13 524
no. of data used in refinement, m	8531
no. of params refined, p	523
$R(F_o)^a$	0.063
$R_w(F_o)^a$	0.084
S^a	1.93
max shift, $(\text{shift/error})_{max}$	0.18
residual extrema in final diff map	+0.987, –0.534

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.06F_o^2)^2]$. $S = [\sum w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$.

vacuum in a 10-cm^3 round bottom flask equipped with a side arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Cyclic voltammetric measurements were performed by using a Princeton Applied Research (PAR) universal programmer (Model 175), potentiostat (Model 173), and digital coulometer (Model 179). The ferrocenium–ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6). The working electrode was a glassy carbon (Atomergic Chemicals V25) electrode with platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported elsewhere.[8]

Crystal Structure Determination. A crystal for complex 3 was obtained by vapor diffusion of diethyl ether into dichloromethane. Diffraction data for 3 were measured on an Enraf-Nonius CAD4 diffractometer with graphite monochromatic Mo Kα radiation. The unit cell dimensions were obtained from a least-squares fit of 25 well-centered reflections. Three checked reflections were monitored every 2 h, and there was no significant variation in intensity during 170 h of data collection. The intensity data were corrected for Lorentz, polarization, and absorption effects. The empirical absorption correction was based on azimuthal (ψ) scans of nine reflections with $80° < \chi < 90°$. Crystal and structure determination data are summarized in Table I. Atomic scattering factors were taken from ref 9. Calculations were carried out on a MicroVax II computer using the Enraf-Nonius SDP program.[10] The structure was solved by direct methods and refined by full matrix least-squares. During the final refinement cycles a list of 523 parameters was refined: atomic coordinates of all the non-hydrogen atoms, isotropic temperature factors for the phenyl carbon atoms, and anisotropic temperature factors for the rest of the non-hydrogen atoms and a scale factor. The methyl hydrogen atoms were omitted while all other hydrogen atoms were included at calculated positions in the structure factor calculation. The final agreement factors are given in Table I. The final atomic coordinates and thermal parameters of the non-hydrogen atoms are collected in Table II. The atomic coordinates of the hydrogen atoms are given in Table SI (supplementary material).

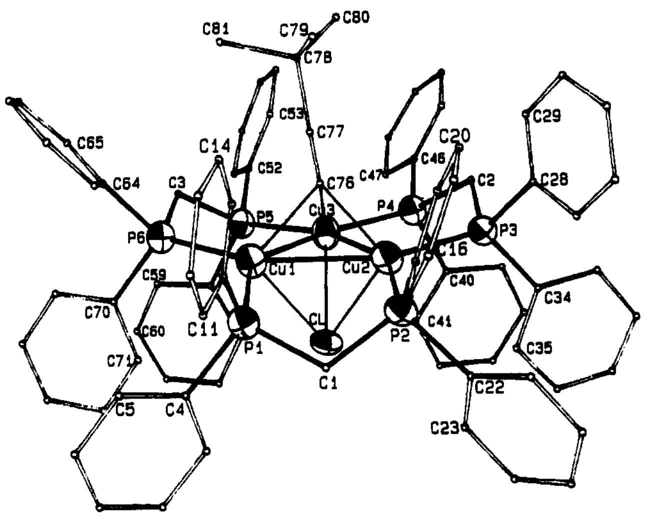

Figure 1. Perspective view of the cation of 3 with atomic numbering.

Results and Discussion

The *triangulo*-Cu_3 complex, $[Cu_3(\mu_3\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3]PF_6$ (1) (dppm = $Ph_2PCH_2PPh_2$) has been prepared according to the literature method[7] by the reaction of the binuclear copper(I) complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ with $PhC{\equiv}CH$ (molar ratio 3:4) in the presence of an excess of KOH in CH_2Cl_2/MeOH (v/v 3:1) under anaerobic and anhydrous conditions. An analogous reaction of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ with $^tBuC{\equiv}CH$ under the same conditions did not give the bicapped *tert*-butylacetylide analogue, $[Cu_3(\mu_3\text{-}C{\equiv}C^tBu)_2(\mu\text{-dppm})_3]PF_6$ (2). Instead, a mixed chloro *tert*-butylacetylide complex, $[Cu_3(\mu_3\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3]PF_6$ (3), was obtained, which has been characterized by X-ray crystallography. However, reaction of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ with $^tBuC{\equiv}CH$ (molar ratio 3:4) in the presence of an excess of KOH in tetrahydrofuran under anaerobic and anhydrous conditions gave 2 quantitatively, isolated as a colorless air-stable solid, the identity of which has been characterized by elemental analyses and NMR spectroscopy.

The IR spectra of 1–3 (Nujol mull, KBr cell) revealed a strong band at ca. 840 cm^{-1} and a medium one at ca. 915 cm^{-1}, characteristic of PF_6^- absorptions. The ^1H NMR spectrum of 2 displayed a methylene resonance as a nonresolved multiplet, indicative of an effective equivalence of the CH_2P_2 protons, similar to that reported for 1.[7] This is consistent with the existence of a formal plane of symmetry containing each Cu_2P_2C moiety arising from the presence of the two $\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu$ ligands on each side of the Cu_3 triangle. This is also in accordance with the inequivalence of the corresponding protons $Cu_2P_2CH_AH_B$ in the related monocapped $[Cu_3(\mu_3\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3](PF_6)_2$ complex,[11] where there is no plane of symmetry and a typical ABX_2 spin system has been observed in the ^1H NMR spectrum.

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Table II. Fractional Coordinates and Thermal Parameters[a] for Non-Hydrogen Atoms and Their Esd's for 3

atom	x	y	z	$B_{eq}/Å^2$	atom	x	y	z	$B_{eq}/Å^2$
Cu(1)	0.12345(8)	0.08343(3)	0.30563(3)	3.28(2)	C(33)	0.1250(6)	0.0282(2)	0.0549(3)	3.6(1)*
Cu(2)	0.08008(7)	0.07791(3)	0.19802(3)	3.12(2)	C(34)	–0.0692(6)	0.1131(2)	0.0738(2)	3.4(1)*
Cu(3)	0.09273(8)	0.16962(3)	0.24001(3)	3.30(2)	C(35)	–0.1843(7)	0.1113(3)	0.0963(3)	4.9(2)*
CL	–0.0921(1)	0.11017(6)	0.25268(6)	3.60(3)	C(36)	–0.2963(9)	0.1186(3)	0.0631(4)	6.6(2)*
P(1)	0.0658(2)	0.00475(6)	0.31648(6)	2.86(3)	C(37)	–0.2887(9)	0.1264(4)	0.0135(4)	6.9(2)*
P(2)	0.0369(2)	–0.00309(5)	0.19842(6)	2.76(3)	C(38)	–0.1811(8)	0.1278(3)	–0.0101(4)	6.4(2)*
P(3)	0.0755(2)	0.10763(5)	0.11590(6)	2.64(3)	C(39)	–0.0634(7)	0.1219(3)	0.0209(3)	4.5(2)*
P(4)	0.0773(2)	0.20803(6)	0.16073(6)	2.84(3)	C(40)	–0.0827(6)	0.2233(2)	0.1344(2)	3.1(1)*
P(5)	0.1166(2)	0.21786(6)	0.31104(6)	2.75(3)	C(41)	–0.1807(7)	0.2222(3)	0.1663(3)	4.8(2)*
P(6)	0.1777(2)	0.12850(6)	0.37773(6)	2.91(3)	C(42)	–0.3037(8)	0.2351(3)	0.1471(3)	5.5(2)*
P(7)	0.3711(2)	0.29684(8)	0.48066(9)	5.44(5)	C(43)	–0.3271(8)	0.2478(3)	0.0965(3)	5.6(2)*
F(1)	0.3176(7)	0.2470(2)	0.4949(3)	12.2(2)	C(44)	–0.2305(7)	0.2485(3)	0.0643(3)	5.0(2)*
F(2)	0.3344(7)	0.2853(3)	0.4233(2)	13.1(2)	C(45)	–0.1081(6)	0.2370(3)	0.0825(3)	3.9(1)*
F(3)	0.4181(6)	0.3484(2)	0.4656(3)	10.3(2)	C(46)	0.1555(6)	0.2658(2)	0.1494(2)	3.1(1)*
F(4)	0.5089(5)	0.2780(3)	0.4778(3)	10.8(2)	C(47)	0.1083(7)	0.3075(3)	0.1718(3)	4.2(1)*
F(5)	0.2331(5)	0.3179(3)	0.4878(3)	11.2(2)	C(48)	0.1644(8)	0.3529(3)	0.1625(3)	5.3(2)*
F(6)	0.4046(5)	0.3086(2)	0.5406(2)	8.1(1)	C(49)	0.2598(8)	0.3561(3)	0.1313(3)	5.8(2)*
C(1)	–0.0299(6)	–0.0182(2)	0.2600(2)	3.1(1)	C(50)	0.3096(8)	0.3170(3)	0.1095(4)	6.2(2)*
C(2)	0.1445(6)	0.1687(2)	0.1128(2)	3.0(1)	C(51)	0.2563(7)	0.2708(3)	0.1182(3)	4.7(2)*
C(3)	0.2234(6)	0.1905(2)	0.3617(3)	3.4(1)	C(52)	0.2042(6)	0.2732(2)	0.2988(2)	3.2(1)*
C(4)	–0.0416(6)	–0.0066(2)	0.3675(3)	3.5(1)*	C(53)	0.3151(7)	0.2668(3)	0.2730(3)	4.5(2)*
C(5)	–0.0000(7)	–0.0253(3)	0.4154(3)	4.9(2)*	C(54)	0.3912(7)	0.3065(3)	0.2622(3)	5.4(2)*
C(6)	–0.0880(8)	–0.0323(3)	0.4538(3)	6.2(2)*	C(55)	0.3554(8)	0.3525(3)	0.2773(3)	5.7(2)*
C(7)	–0.2101(8)	–0.0217(3)	0.4431(3)	6.1(2)*	C(56)	0.2464(7)	0.3582(3)	0.3012(3)	5.1(2)*
C(8)	–0.2526(9)	–0.0020(3)	0.3969(4)	6.6(2)*	C(57)	0.1711(7)	0.3197(3)	0.3129(3)	4.3(1)*
C(9)	–0.1678(7)	0.0063(3)	0.3583(3)	4.9(2)*	C(58)	–0.0199(6)	0.2363(2)	0.3460(2)	3.2(1)*
C(10)	0.1904(6)	–0.0409(2)	0.3261(3)	3.6(1)*	C(59)	–0.0070(7)	0.2568(3)	0.3950(3)	4.3(1)*
C(11)	0.1667(7)	–0.0878(3)	0.3424(3)	5.1(2)*	C(60)	–0.1137(8)	0.2668(3)	0.4208(3)	5.6(2)*
C(12)	0.2637(9)	–0.1228(4)	0.3461(4)	7.2(2)*	C(61)	–0.2285(8)	0.2572(3)	0.3997(3)	5.8(2)*
C(13)	0.3825(9)	–0.1091(4)	0.3343(4)	7.1(2)*	C(62)	–0.2474(8)	0.2375(3)	0.3507(3)	5.7(2)*
C(14)	0.4086(9)	–0.0634(4)	0.3181(4)	7.0(2)*	C(63)	–0.1401(7)	0.2260(3)	0.3242(3)	4.4(1)*
C(15)	0.3104(7)	–0.0289(3)	0.3138(3)	5.1(2)*	C(64)	0.3196(6)	0.1079(2)	0.4172(2)	3.4(1)*
C(16)	0.1569(6)	–0.0489(2)	0.1890(3)	3.3(1)*	C(65)	0.3990(7)	0.1392(3)	0.4450(3)	5.0(2)*
C(17)	0.1363(7)	–0.0975(3)	0.2009(3)	4.9(2)*	C(66)	0.5039(8)	0.1215(3)	0.4761(3)	6.0(2)*
C(18)	0.2255(9)	–0.1328(3)	0.1884(4)	6.4(2)*	C(67)	0.5275(7)	0.0725(3)	0.4759(3)	5.0(2)*
C(19)	0.3318(9)	–0.1186(3)	0.1649(4)	6.5(2)*	C(68)	0.4499(7)	0.0421(3)	0.4487(3)	5.0(2)*
C(20)	0.3541(8)	–0.0718(3)	0.1534(4)	6.1(2)*	C(69)	0.3448(6)	0.0592(3)	0.4197(3)	4.1(1)*
C(21)	0.2653(7)	–0.0360(3)	0.1665(3)	4.8(2)*	C(70)	0.0593(6)	0.1349(2)	0.4254(2)	3.2(1)*
C(22)	–0.0962(6)	–0.0222(2)	0.1535(2)	3.2(1)*	C(71)	–0.0629(7)	0.1216(3)	0.4107(3)	4.6(2)*
C(23)	–0.2137(7)	–0.0006(3)	0.1586(3)	4.3(1)*	C(72)	–0.1584(8)	0.1248(3)	0.4457(3)	5.7(2)*
C(24)	–0.3191(7)	–0.0144(3)	0.1266(3)	4.7(2)*	C(73)	–0.1263(8)	0.1407(3)	0.4947(3)	6.1(2)*
C(25)	–0.3074(7)	–0.0496(3)	0.0907(3)	5.2(2)*	C(74)	–0.0069(8)	0.1545(3)	0.5103(3)	5.4(2)*
C(26)	–0.1923(8)	–0.0699(3)	0.0832(3)	5.3(2)*	C(75)	0.0883(7)	0.1518(3)	0.4756(3)	4.4(1)*
C(27)	–0.0845(7)	–0.0571(3)	0.1146(3)	4.2(1)*	C(76)	0.2326(4)	0.1098(2)	0.2426(2)	1.43(9)
C(28)	0.1778(5)	0.0697(2)	0.0785(2)	2.8(1)*	C(77)	0.3380(8)	0.1093(2)	0.2466(3)	4.3(2)
C(29)	0.3065(6)	0.0775(2)	0.0779(3)	3.7(1)*	C(78)	0.4868(7)	0.1082(3)	0.2491(4)	5.5(2)
C(30)	0.3842(7)	0.0441(3)	0.0543(3)	4.4(1)*	C(79)	0.537(1)	0.0571(5)	0.2400(8)	16.5(6)
C(31)	0.3307(7)	0.0031(3)	0.0319(3)	4.5(1)*	C(80)	0.533(1)	0.1401(7)	0.2109(7)	21.9(5)
C(32)	0.2020(7)	–0.0044(3)	0.0315(3)	4.6(2)*	C(81)	0.541(1)	0.1189(7)	0.3067(6)	16.1(6)

[a] Starred values refer to atoms that were refined isotropically. $B_{eq} = {}^1/_3\sum_i\sum_j B_{ij}(a_i^*a_j^*)\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 3

Cu(1)–Cu(2)	2.791(2)	Cu(1)–Cu(3)	2.927(2)
Cu(2)–Cu(3)	2.754(2)	Cu(1)–C(76)	2.187(5)
Cu(2)–C(76)	2.105(4)	Cu(3)–C(76)	2.213(5)
Cu(1)–Cl	2.675(2)	Cu(2)–Cl	2.543(2)
Cu(3)–Cl	2.589(2)	C(76)–C(77)	1.12(1)
Cu(1)–Cu(2)–Cu(3)	63.71(3)	Cu(1)–Cu(3)–Cu(2)	58.80(3)
Cu(2)–Cu(1)–Cu(3)	57.50(3)	Cu(1)–C(76)–Cu(2)	81.2(2)
Cu(1)–C(76)–Cu(3)	83.4(2)	Cu(2)–C(76)–Cu(3)	79.3(1)
Cu(1)–Cl–Cu(2)	64.60(4)	Cu(1)–Cl–Cu(3)	67.50(4)
Cu(2)–Cl–Cu(3)	64.91(4)	C(76)–C(77)–C(78)	176.9(7)

A perspective drawing of the X-ray crystal structure of 3 with atomic numbering is depicted in Figure 1. Selected bond distances and angles are listed in Table III. The complex consists of an isosceles triangular array of copper atoms with a dppm ligand bridging each edge to form a roughly planar $[Cu_3P_6]^+$ core. The bridging mode of the alkynyl group is asymmetric with the Cu—C bond distances in the range 2.105(4)–2.213(5) Å and the bond angles between the alkynyl group and each copper atom (Cu—C(76)—C(77)) in the range 120.2(5)–140.2(5)°. The linearity of the *tert*-butylacetylide group (C(76)—C(77)—C(78)) = 176.9(7)°) and the bond distance of the C≡C bond (1.12(1) Å) are characteristic of typical metal–acetylide σ bonding. A similar bonding mode has been found in the analogous complex 1.[7]

The electronic absorption spectra of complexes 1–3 in MeCN exhibit intense low energy absorption bands in the 300–350-nm region (Figure 2). Excitation of a solid sample of 1–3 at λ > 350 nm both at 77 K and at room temperature produce long-lived intense luminescence. The photophysical data are summarized in Table IV. Emission was also observed at room temperature in a fluid solution of MeCN. The solid-state emission spectra of all the three complexes 1–3 showed very similar patterns, a high energy band at ca. 440–485 nm and a lower energy emission at ca. 525–540 nm. The high energy emission at ca. 440–485 nm is likely to be metal to ligand charge transfer in nature [$Cu \rightarrow \pi^*(RC{\equiv}C^-)$] since complexes 2 and 3 emit at similar energies (450 nm for 2 vs 440 nm for 3) while emission of 1 occurs at lower energy (485 nm), consistent with the lower π* energy level for the phenylacetylide moiety. A

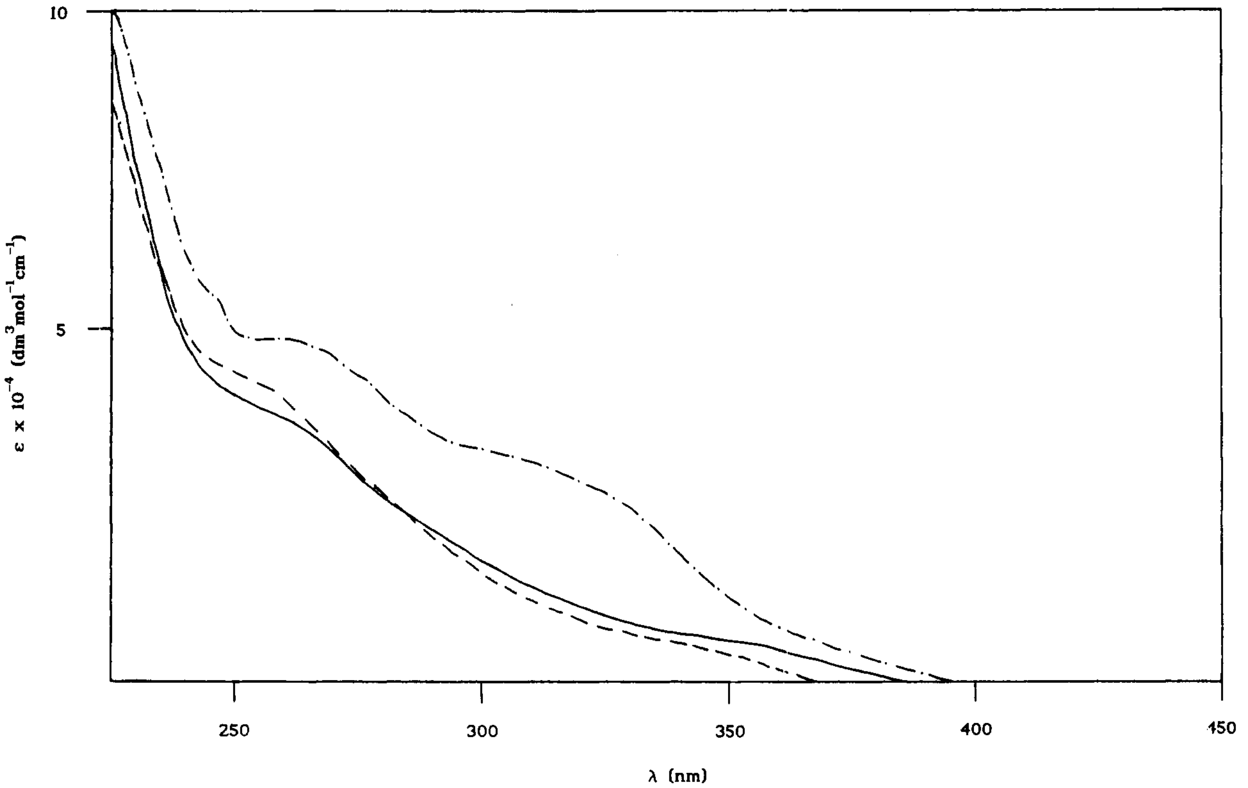

Figure 2. Electronic absorption spectra of 1 (– • –), 2 (—), and 3 (- - -) in MeCN.

Table IV. Photophysical Data for Compounds 1–3

compd	medium (temp/K)	λ/nm (τ_0/μs)
1	solid (298)	493 (14 ± 1)
	solid (77)	485, 525 (sh)
	^{n}PrCN glass (77)	471, 500 (sh)
	MeCN (298)	494 (6.5 ± 0.6)[a]
2	solid (298)	450 (0.44 ± 0.05) 540 (1.7 ± 0.2)
	solid (77)	450, 530 (sh)
	^{n}PrCN glass (77)	442, 500 (sh)
	MeCN (298)	456 (0.27 ± 0.03)[a] 600sh (4.1 ± 0.4)[a]
3	solid (298)	440 (sh) (<0.01) 535 (33 ± 3)
	solid (77)	440, 572
	MeCN (298)	540 (sh) (5.3 ± 0.5)[a] 613 (5.4 ± 0.5)[a]

[a] [Cu_3] ≃ 0.2 mM.

similar emission band at ca. 483 nm has also been observed in a tetranuclear $Cu_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4(PPh_3)_4$ complex.[12] For complex 2, the luminescence at 540 nm in the solid state was red-shifted to ca. 600 nm in MeCN (Figure 3) with a lifetime of 4.1 μs. The long lifetime of emission suggests that the emission is most likely associated with a spin-forbidden transition. We suggest that the low energy emitting state is related to the metal-centered excited state $3d^94s^1$ of Cu(I). With the short Cu—Cu distances ranging from 2.570(3) to 2.615(3) Å in 1[7] and 2.754(2) to 2.791(2) Å in 3, it follows that the emitting $3d^94s^1$ state of Cu(I) should be strongly modified by the copper—copper interaction in the trimer. With reference to previous works on tetrameric d^{10} metal complexes,[2a–j] some net bonding for the filled d orbitals can result by a configuration interaction of these MO's of d parentage with appropriate empty orbitals derived from the higher energy 4s and 4p atomic orbitals of the Cu_3 unit. Similar configuration interaction has been suggested for the analogous binuclear d^8 metal complexes.[13] The lowest energy transition of the Cu_3 core may involve the promotion of an electron from an antibonding d orbital to an empty bonding s orbital at higher energies. The excited state thus formed is expected to be strongly contracted and distorted as a result of an increase of Cu—Cu bonding in the excited state. The red shift for the luminescence in solution can be attributed to rigidochromic effects where larger structural changes can take place in solution but not in the rigid lattice of the solid. Similar red shifts have also been reported for d^{10} metal clusters.[2] Another possible assignment of the origin of the low energy emission would be a RC≡C → Cu_3 acetylide-to-metal charge-transfer excited state, as suggested by Ford and co-workers for the tetrameric iodocopper(I) clusters based on ab initio calculations.[2d] Since the LUMO would remain σ-bonding with regard to the Cu_3 core, this excited state would also be expected to display substantial distortion from the ground-state configuration. However, we favor the assignment of d → s origin over the RC≡C → Cu_3 assignment since the low energy emission occurs at similar energies for complexes 1–3, irrespective of the nature of the acetylide.

The cyclic voltammograms of both 1 and 2 in MeCN (0.1 mol dm^{-3} $^nBu_4NPF_6$) show a quasi-reversible oxidation couple at ca. +0.41 and +0.37 V vs the ferrocenium–ferrocene couple, respectively, assignable to a one-electron oxidation at the Cu^I center. The slightly greater ease of oxidation of 2 than 1 is consistent with the greater σ-donating ability of the *tert*-butylacetylide group over its phenyl counterpart. Further oxidation of these clusters

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(12) Yam, V. W. W. Unpublished results.

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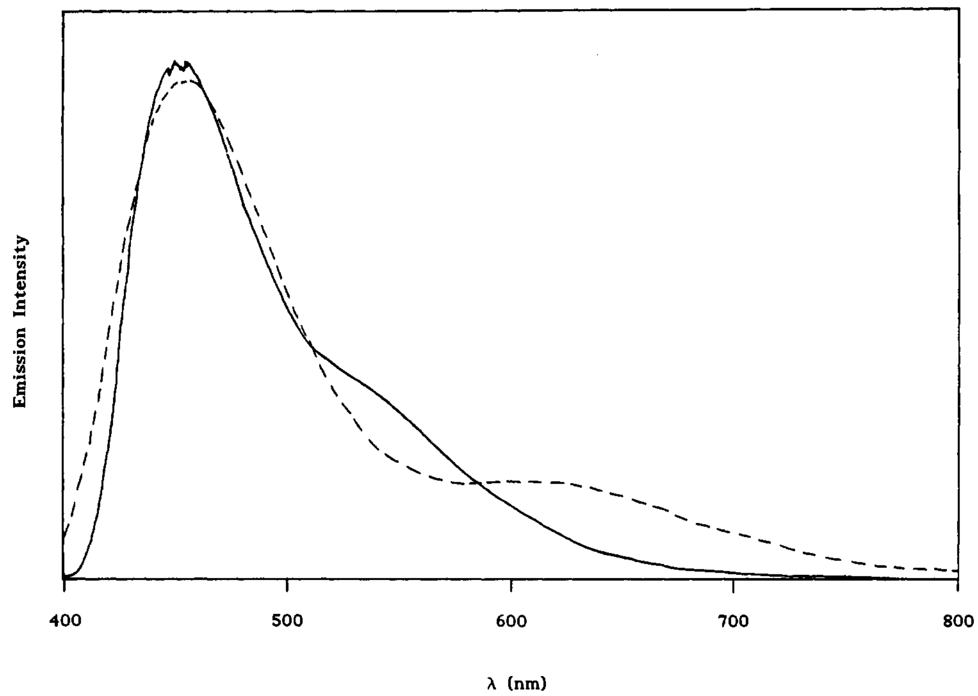

Figure 3. Emission spectra of **2** in the solid state at 77 K (—) and in degassed MeCN at 298 K (- - -).

might result in decomposition, as suggested by the irreversibility of the couples at more anodic potentials.

The present work offers an opportunity to study the luminescent properties of trimeric organocopper(I) clusters where rich photochemistry and their potential applications in organic transformation are anticipated as a result of their strong reducing power in the excited state. Work is in progress to investigate a series of related trinuclear and tetranuclear clusters with various acetylides and phosphine ligands for reactivity tuning as well as for systematic comparison studies.

Acknowledgment. V.W.W.Y. acknowledges support from the Research Grants Council and the University of Hong Kong. W.K.L. acknowledges the receipt of a studentship, administered by the University of Hong Kong.

Supplementary Material Available: Tables of hydrogen atom coordinates (Table SI), general displacement parameter expressions, *U* (Table SII), complete bond distances (Table SIII), and complete bond angles (Table SIV) (7 pages). Ordering information is given on any current masthead page.

OM9207119