

Syntheses, Photophysics, and X-ray Structural Characterization of Dinuclear Platinum(II) Acetylide Complexes, $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-PhC}\equiv\text{C})(\text{PhC}\equiv\text{C})_2]\text{ClO}_4$ and $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-}^t\text{BuC}\equiv\text{C})(^t\text{BuC}\equiv\text{C})\text{Cl}]\text{ClO}_4$

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Refluxing an ethanolic solution of $[\text{Pt}(\text{dppm-}P,P')]\text{Cl}_2$ with $\text{Hg}(\text{PhC}\equiv\text{C})_2$ in ethanol gave air-stable $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-PhC}\equiv\text{C})(\text{PhC}\equiv\text{C})_2]^+$ as the major product, isolated as the Cl^- or ClO_4^- (1) salt. A similar reaction with $\text{Hg}(^t\text{BuC}\equiv\text{C})_2$ gave $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-}^t\text{BuC}\equiv\text{C})(^t\text{BuC}\equiv\text{C})\text{Cl}]^+$ instead, also isolated as the Cl^- or ClO_4^- (2) salt. The crystal structures of 1 and 2 have been determined by X-ray diffraction. Compound 1 crystallizes in the monoclinic space group $C2/c$ with $Z = 4$ in a unit cell of dimensions $a = 27.942(7)$ Å, $b = 11.218(4)$ Å, $c = 25.720(7)$ Å, and $\beta = 124.22(2)^\circ$. Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 11.783(3)$ Å, $b = 12.791(3)$ Å, $c = 21.210(7)$ Å, $\alpha = 89.11(3)^\circ$, $\beta = 77.41(2)^\circ$, and $\gamma = 71.50(2)^\circ$. Both structures have been solved by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 5203 observed reflections to R and R_w values of 0.038 and 0.048 for 1 and 9724 observed reflections to R and R_w values of 0.033 and 0.044 for 2, respectively. Both complexes have been found to exhibit long-lived photoluminescence both in the solid state and in fluid solutions (solid-state emission: 1, $\lambda_{\text{em}} = 618$ nm, $\tau_0 = 2.2 \pm 0.2$ μs; 2, $\lambda_{\text{em}} = 621$ nm, $\tau_0 = 3.5 \pm 0.3$ μs). The phosphorescent state of 1 has been shown to be quenched by pyridinium acceptors.

Introduction

There has been a long-standing interest in luminescent Pt complexes. Recent work on the well-known $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ ($\text{Pt}_2(\text{POP})_4^{4-}$) has led to a surge of interest in novel luminescent materials based on the binuclear d^8 - d^8 metal core.¹ To our knowledge, these metal dimers are mainly confined to geometries having stacked face-to-face square planes, although A-frame pyrazolyl-bridged complexes of Rh(I) and Ir(I) are known.^{1b-k} As part of our research program to search for novel luminescent binuclear metal complexes for photochemical C—H bond activation, we have successfully synthesized the first example of homobimetallic Pt(II) $\mu\text{-RC}\equiv\text{C}$ A-frame complexes, $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-PhC}\equiv\text{C})(\text{PhC}\equiv\text{C})_2]\text{ClO}_4$ (1) and $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-}^t\text{BuC}\equiv\text{C})(^t\text{BuC}\equiv\text{C})\text{Cl}]\text{ClO}_4$ (2), which are shown to exhibit long-lived intense luminescence at room temperature. Despite numerous reported examples of A-frame complexes of Pt(I),² A-frame complexes of homobimetallic Pt(II) are rare and are mainly confined to those containing a $\mu\text{-H}$ bridgehead.³ A-frame examples of Pt(II) containing $\mu\text{-RC}\equiv\text{C}$ bridgeheads have only been reported for heterobimetallic systems.⁴ We report here the syntheses, spectroscopy, and the X-ray crystal structures of complexes 1 and 2.

Experimental Section

Materials and Reagents. The ligand bis(diphenylphosphino)methane (dppm) was obtained from Strem Chemicals, Inc. $\text{Pt}(\text{cod})\text{Cl}_2$ was purchased from Johnson Matthey Co. $[\text{Pt}(\text{dppm-}P,P')]\text{Cl}_2$ was prepared by the literature method.^{2c} Phenylacetylene and 3,3-dimethylbut-1-yne were obtained from Aldrich Chemical Co. Acetonitrile was purified and distilled using standard procedures before use.⁵ All other solvents and reagents were of analytical grade and were used as received.

Syntheses of Platinum Complexes. $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-PhC}\equiv\text{C})(\text{PhC}\equiv\text{C})_2]\text{X}$ ($\text{X} = \text{Cl}$ or ClO_4) (1). Phenylacetylene (0.038 g, 0.37 mmol) was added to a solution of mercury(II) acetate (0.0624 g, 0.20 mmol) in ethanol (8 cm³) and the resultant solution added to a solution of $[\text{Pt}(\text{dppm-}P,P')]\text{Cl}_2$ (0.20 g, 0.19 mmol) in ethanol (10 cm³). The mixture was then heated under reflux for 24 h, cooled, and filtered. The orange filtrate was evaporated to dryness under reduced pressure. The residue was extracted into dichloromethane, which was then filtered, and upon addition of diethyl ether to the filtrate, orange crystals of $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-PhC}\equiv\text{C})(\text{PhC}\equiv\text{C})_2]\text{Cl}$ were obtained. A metathesis reaction

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to yield the perchlorate salt could be accomplished by dissolving the Cl⁻ salt in methanol, followed by addition of lithium perchlorate to give [Pt₂(μ-dppm)₂(μ-PhC≡C)(PhC≡C)₂]ClO₄. Orange crystals of [Pt₂(μ-dppm)₂(μ-PhC≡C)(PhC≡C)₂]ClO₄ could be obtained by slow diffusion of diethyl ether vapor into an acetonitrile solution of the salt. Yield: 0.09 g (60%). IR (Nujol mull): ν(C≡C) 2120 cm⁻¹. UV/vis (MeCN), λ/nm (ε_{max}/dm³ mol⁻¹ cm⁻¹): 265 (sh) (54 210), 393 (18 170), 450 (sh) (7180). UV/vis (CH₂Cl₂) λ/nm (ε_{max}/dm³ mol⁻¹ cm⁻¹): 397 (16 980), 450 (sh) (6170). ¹H NMR (CD₃CN): δ 4.54 (m, -CH₂-, 4H), 6.5–7.5 (m, phenyl protons of dppm, 40H), 7.84 (m, phenyl protons of acetylide, 15H). ³¹P NMR (CD₃CN): δ 3.01 (¹J(PtP) = 2468 Hz). Anal. Calcd for C₇₄H₆₉ClO₄P₄Pt₂·H₂O: C, 56.23; H, 3.89; Cl, 2.25. Found: C, 56.3; H, 3.54; Cl, 2.20.

[Pt₂(μ-dppm)₂(μ-BuC≡C)(^tBuC≡C)Cl]X (X = Cl or ClO₄) (2). The procedure is similar to that described for the preparation of 1 except 3,3-dimethylbut-1-yne (0.030 g, 0.37 mmol) was used in place of phenylacetylene. Orange crystals of [Pt₂(μ-dppm)₂(μ-BuC≡C)(^tBuC≡C)Cl]ClO₄ could be obtained by slow diffusion of diethyl ether vapor into an acetonitrile solution of the salt. Yield: 0.06 g (43%). IR (Nujol mull): ν(C≡C) 2100 cm⁻¹. UV/vis (MeCN), λ/nm (ε_{max}/dm³ mol⁻¹ cm⁻¹): 265 (sh) (28 720), 357 (9430). UV/vis (CH₂Cl₂) λ/nm (ε_{max}/dm³ mol⁻¹ cm⁻¹): 265 (34 540), 358 (10 230). ¹H NMR (CD₃CN): δ 0.64 (s, (CH₃)₃C-, 18H), 4.12 (m, -CH₂-, 4H), 7.3–8.2 (m, phenyl protons of dppm, 40H). ³¹P NMR (CD₃CN): δ 1.84. Anal. Calcd for C₆₂H₆₂Cl₂O₄P₄Pt₂: C, 51.11; H, 4.29. Found: C, 50.80; H, 4.16.

Physical Measurements and Instrumentation. UV-visible spectra were obtained on a Milton Roy Spectronic 8000 diode array spectrophotometer, IR spectra were obtained as Nujol mulls on a Shimadzu IR-470 infrared spectrophotometer (4000–400 cm⁻¹), 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. ¹H NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer with chemical shifts reported relative to TMS. ³¹P NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform NMR spectrometer with chemical shifts reported relative to H₃PO₄. Elemental analyses of the new complexes were performed by the Shanghai Institute of Organic Chemistry, Academia Sinica.

Luminescence quantum yields, φ, were measured at room temperature by the Parker-Rees method using quinine sulfate (φ = 0.546) as a standard.⁸ 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 vacuum in a 10-cm³ 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. Bimolecular quenching experiments were monitored by emission measurements in MeCN (0.1 mol dm⁻³ NBu₄PF₆), and data were treated by a Stern-Volmer fit as described by I₀/I = 1 + k_qτ₀[Q] where I₀ and I are the respective emission intensities in the absence and in the presence of various quencher concentrations, [Q], and k_q is the bimolecular quenching rate constant.

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 NBu₄PF₆). 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.⁷

Table I. Crystal and Structure Determination Data for Compounds 1 and 2

	compd 1	compd 2
formula	Pt ₂ C ₇₄ H ₆₉ P ₄ ClO ₄	Pt ₂ C ₆₂ H ₆₂ Cl ₂ P ₄ ClO ₄
fw	1561.81	1456.16
T, °C	23	24
a, Å	27.942(7)	11.783(3)
b, Å	11.218(4)	12.791(3)
c, Å	25.720(7)	21.210(7)
α, deg		89.11(3)
β, deg	124.22(2)	77.41(2)
γ, deg		71.50(2)
V, Å ³	6667(5)	2954(2)
cryst syst	monoclinic	triclinic
space group	C2/c	P1
Z	4	2
F(000)	3072	1432
ρ _{calcd} , g cm ⁻³	1.556	1.637
cryst color/shape	orange prism	yellow tablet
cryst dimens, mm	0.18 × 0.28 × 0.28	0.12 × 0.35 × 0.35
λ, Å (graphite monochromated, Mo Kα)		0.710 73
μ, cm ⁻¹	44.2	50.2
transm factors	0.801–0.999	0.506–0.999
collcn range	2θ _{max} = 53°; ±h,k,l	2θ _{max} = 53°; h,±k,±l
scan mode and scan speed, deg min ⁻¹	ω-2θ; 1.00–5.49	ω-2θ; 1.37–8.24
scan width, deg	0.70 + 0.34 tan θ	0.60 + 0.34 tan θ
bckgd time		0.5 × scan time
no. of data colld	7422	12783
no. of unique data	7258	12175
no. of data used in refinement, m	5203 (F _o > 3σ(F _o))	9724 (F _o > 3σ(F _o))
no. of params refined, p	335	637
R(F _o) ^a	0.038	0.033
R _w (F _o) ^a	0.048	0.044
S ^a	1.589	1.545
max shift, (shift/error) _{max}	0.05	0.01
residual extrema in final diff map	0.82, -1.27	1.38, -1.24

$$^a R = \sum |F_o - F_c| / \sum F_o; R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}, \text{ with } w = 4F_o^2 / [\sigma^2(F_o^2) + (0.04F_o^2)^2]; S = [\sum w(F_o - F_c)^2 / (m - p)]^{1/2}.$$

Crystal Structure Determination. Crystals for 1 and 2 were obtained by vapor diffusion of diethyl ether into acetonitrile. Diffraction data for [Pt₂(dppm)₂(PhC≡C)₂]ClO₄ (1) and [Pt₂(dppm)₂(^tBuC≡C)₂]ClO₄ (2) were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The unit cell dimensions were obtained from a least-squares fit of 25 well-centered reflections. 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° < ψ < 90°. Three check reflections were monitored every 2 h; for the data of compound 1, which showed a gradual decrease in intensity to a maximum of 10.8% at the end of 89 h, correction for linear decay was also applied. Crystal and structure determination data are summarized in Table I. Atomic scattering factors were taken from ref 8. Calculations were carried out on a MicroVax II computer using the Enraf-Nonius SDP program.⁹

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. The analysis of compound 2 was straightforward: the methyl carbon atoms were refined isotropically while all other non-hydrogen atoms anisotropically; the hydrogen atoms, except those in the methyl groups, which were omitted, were included at calculated positions in the structure factor calculations only. Final agreement factors are given in Table I.

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The analysis of compound 1 was somewhat complicated. From the systematic absences the space group could be either $C2/c$ or Cc and the space group $C2/c$ was first assumed. The fragment $Pt_2(dppm)_2(PhC\equiv C)_2$ in the cation was first located with half a fragment in one asymmetric unit and the other half related to the first by a 2-fold symmetry. However, when the third $PhC\equiv C$ group was located, the ethylene C atom formed a σ bond with one Pt atom and the Pt-C-C angle was close to 180° , hence no C_2 symmetry possessed by the cation. Since there are only four formula units per unit cell, the space group was changed to Cc but the refinement did not converge and led to a number of unreasonable bond lengths and angles in the phenyl rings. The space group $C2/c$ was tried again on the assumption that there was packing disordered so that on average the third $PhC\equiv C$ group alternated between the two Pt atoms; this was further supported by the fact that electron densities corresponding to atoms in this group were much lower than those of other C atoms. The Cl atom in the perchlorate group was located at an inversion center with two sets of disordered O atoms related to each other by a center of symmetry. With the proposed model the refinement converged. In the final refinement cycles, a list of 335 parameters was adjusted: coordinates of all the non-hydrogen atoms, anisotropic temperature factors for atoms in the $Pt(dppm)$ and $C(34)$ in the $PhC\equiv C$ group, isotropic temperature factors for the rest of the non-hydrogen atoms, and a scale factor. The hydrogen atoms of the dppm group were included in the structure factor calculation at calculated positions and other hydrogen atoms were omitted. The final R factors are given in Table I. The final atomic coordinates and thermal parameters of the non-hydrogen atoms for compounds 1 and 2 are collected in Tables II and III, respectively. The atomic coordinates of the hydrogen atoms for compounds 1 and 2 are given in Tables SI and SVI, respectively (supplementary material).

Results and Discussion

Refluxing an ethanolic solution of $[Pt(dppm-P, P')_2]Cl_2$ with $Hg(PhC\equiv C)_2$, prepared from $PhC\equiv CH$ and $Hg(CH_3COO)_2$ in ethanol, to our surprise gave $[Pt_2(\mu-dppm)_2(\mu-PhC\equiv C)(PhC\equiv C)_2]Cl$ as the major product instead, with $[Pt_2(\mu-dppm)_2(PhC\equiv C)_2HgCl_2]$ as the minor product which could easily be removed by filtration. A metathesis reaction to yield the perchlorate salt could be accomplished by dissolving the Cl⁻ salt in methanol, followed by addition of lithium perchlorate to give $[Pt_2(\mu-dppm)_2(\mu-PhC\equiv C)(PhC\equiv C)_2]ClO_4$ (1), obtained as orange crystals. A similar reaction was reported by Shaw and co-workers with a much shorter reflux time to give $[Pt_2(\mu-dppm)_2(PhC\equiv C)_2HgCl_2]$ (literature yield: 88%) as the product.¹⁰ Attempts to prepare the *tert*-butylacetylide analogue did not give $[Pt_2(\mu-dppm)_2(\mu-tBuC\equiv C)(tBuC\equiv C)_2]^+$ but instead gave orange crystals of $[Pt_2(\mu-dppm)_2(\mu-tBuC\equiv C)(tBuC\equiv C)Cl]Cl$, which could be obtained as the perchlorate salt via a metathesis reaction to give $[Pt_2(\mu-dppm)_2(\mu-tBuC\equiv C)(tBuC\equiv C)Cl]ClO_4$ (2).

The IR data ($\nu(C\equiv C)$): 1, 2120 cm^{-1} ; 2, 2100 cm^{-1} are consistent with the presence of a terminal $C\equiv C$ bond in the products. An intense IR stretch at ca. 1100 cm^{-1} is observable in the spectra for the perchlorate salts of 1 and 2, assigned as the $\nu(Cl-O)$ stretch. Complexes 1 and 2 are air-stable solids, which can be stored indefinitely.

X-ray Crystal Structure Studies. Figures 1 and 2 show the perspective drawings of the cations of 1 and 2, respectively. Selected bond distances and angles are given in Tables IV and V. The structure of complex 1 is very close to a regular A-frame with terminal phenylacetylide

Table II. Fractional Coordinates and Thermal Parameters^a of Non-Hydrogen Atoms and Their Esd's in Compound 1

atom	x	y	z	$B_{eq}, \text{\AA}^2$
Pt	0.02543(1)	0.09099(2)	0.20692(1)	3.655(4)
Cl	0.250	0.250	0.000	14.6(2)*
P(1)	-0.07010(5)	0.1065(1)	0.12301(5)	3.93(3)
P(2)	0.11859(5)	0.0724(2)	0.29474(6)	4.19(3)
O(1)	0.3135(5)	0.255(1)	0.0525(6)	11.5(4)*
O(2)	0.2378(7)	0.125(2)	-0.0278(7)	14.2(5)*
O(3)	0.2517(8)	0.328(2)	-0.0434(8)	17.4(7)*
O(4)	0.2238(7)	0.268(2)	0.0282(8)	17.3(7)*
C(1)	-0.1197(2)	0.0277(6)	0.1360(2)	4.7(1)
C(2)	-0.0982(2)	0.2556(6)	0.1019(2)	5.0(1)
C(3)	-0.1550(3)	0.2743(7)	0.0523(3)	6.5(2)
C(4)	-0.1775(3)	0.3864(8)	0.0362(4)	8.6(3)
C(5)	-0.1430(3)	0.4820(8)	0.0688(4)	9.9(3)
C(6)	-0.0877(3)	0.4675(8)	0.1162(4)	9.8(3)
C(7)	-0.0646(3)	0.3528(7)	0.1343(3)	6.8(2)
C(8)	-0.0845(2)	0.0435(6)	0.0506(2)	4.9(1)
C(9)	-0.1108(3)	-0.0635(8)	0.0271(3)	8.7(2)
C(10)	-0.1192(4)	-0.1084(8)	-0.0280(4)	10.3(3)
C(11)	-0.0985(3)	-0.0485(9)	-0.0563(3)	8.9(2)
C(12)	-0.0741(3)	0.0560(9)	-0.0359(3)	8.8(2)
C(13)	-0.0660(3)	0.1069(8)	0.0189(3)	7.6(2)
C(14)	0.1561(2)	-0.0456(7)	0.2836(3)	6.1(2)
C(15)	0.1813(3)	-0.1417(8)	0.3220(4)	9.2(2)
C(16)	0.2090(4)	-0.227(1)	0.3103(5)	13.6(4)
C(17)	0.2091(4)	-0.216(1)	0.2570(5)	13.8(4)
C(18)	0.1860(4)	-0.120(1)	0.2198(4)	16.8(4)
C(19)	0.1592(3)	-0.032(1)	0.2321(3)	11.5(3)
C(20)	0.1670(2)	0.1984(6)	0.3214(2)	4.7(1)
C(21)	0.2259(2)	0.1834(8)	0.3610(3)	7.0(2)
C(22)	0.2623(3)	0.281(1)	0.3843(3)	8.9(3)
C(23)	0.2412(3)	0.3934(8)	0.3688(4)	8.6(2)
C(24)	0.1830(3)	0.4097(7)	0.3296(3)	7.8(2)
C(25)	0.1462(2)	0.3120(7)	0.3060(3)	5.9(2)
C(26)	0.0499(2)	0.2050(5)	0.1685(2)	4.4(1)*
C(27)	0.0657(2)	0.2685(6)	0.1446(3)	5.1(1)*
C(28)	0.0857(3)	0.3485(8)	0.1161(3)	7.0(2)*
C(29)	0.0546(4)	0.376(1)	0.0553(5)	11.4(3)*
C(30)	0.0749(5)	0.450(1)	0.0262(6)	13.6(4)*
C(31)	0.1258(5)	0.504(1)	0.0671(6)	14.9(4)*
C(32)	0.1597(7)	0.464(2)	0.1228(8)	19.6(6)*
C(33)	0.1433(5)	0.382(1)	0.1520(5)	12.2(4)*
C(34)	0.000	-0.0276(8)	0.250	5.0(2)
C(35) ^b	-0.0116(4)	-0.100(1)	0.2698(5)	4.6(2)*
C(36) ^b	-0.0243(4)	-0.207(1)	0.2903(5)	4.9(3)*
C(37) ^b	-0.0386(7)	-0.305(2)	0.2515(8)	10.2(5)*
C(38) ^b	-0.054(1)	-0.420(2)	0.270(1)	12.2(7)*
C(39) ^b	-0.057(1)	-0.416(2)	0.319(1)	11.8(7)*
C(40) ^b	-0.0443(8)	-0.320(2)	0.3586(8)	10.8(6)*
C(41) ^b	-0.0274(6)	-0.211(2)	0.3409(7)	8.1(4)*

^a $B_{eq} = 1/3 \sum_i \sum_j B_{ij}(a_i^* a_j^*) a_i a_j$. Starred entries refer to atoms refined isotropically. ^b Occupancy factor = 0.5.

and bridging dppm ligands and a bridgehead $\mu_2-\eta^2$ $PhC\equiv C$ group. The intramolecular Pt...Pt distances of 3.236(1) Å in 1 and 3.15(1) Å in 2 are similar to those found in $[Pt_2(dppm)_2(CN)_4]$ (3.301(1) Å)^{1c} and other Pt(I) A-frame complexes such as $[Pt_2Cl_2(\mu-NO)(\mu-dppm)_2]^+$ (3.246(3) Å).^{2d} For square-planar Pt(II) complexes consisting of monomeric units stacked to form a continuous chain of metal atoms, the intermolecular Pt...Pt distances lie in the range 3.09–3.50 Å.¹¹ Although the Pt...Pt distances of 3.236(1) Å in 1 and 3.151(1) Å in 2 are somewhat longer than that for $[Pt_2(pop)_4]^{4+}$ (2.925(1) Å),¹² they are still indicative of weak Pt...Pt interactions.

Both complexes 1 and 2 show a slightly distorted square-planar coordination about each Pt atom, with 2 showing a slightly greater distortion. In 1, the bond angles

(11) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* 1976, 20, 1 and references therein.

(12) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr., Sect. B* 1983, 39, 280.

Table III. Fractional Coordinates and Thermal Parameters^a of Non-Hydrogen Atoms and Their Esd's for Compound 2

atom	x	y	z	$B_{eq}, \text{\AA}^2$	atom	x	y	z	$B_{eq}, \text{\AA}^2$
Pt(1)	0.15743(2)	0.17028(1)	0.25305(1)	2.506(4)	C(31)	0.5050(6)	-0.1943(6)	0.4344(3)	6.0(2)
Pt(2)	0.44160(2)	0.11224(1)	0.24335(1)	2.499(4)	C(32)	0.4748(6)	-0.1777(5)	0.3755(3)	4.7(2)
Cl(1)	0.6122(1)	0.0808(1)	0.15790(8)	4.29(3)	C(33)	0.5799(4)	-0.1765(4)	0.2019(3)	3.0(1)
P(1)	0.1348(1)	0.3559(1)	0.26432(7)	2.94(3)	C(34)	0.5861(5)	-0.1676(5)	0.1368(3)	3.9(1)
P(2)	0.2026(1)	-0.0168(1)	0.23122(6)	2.61(3)	C(35)	0.6749(6)	-0.2438(6)	0.0923(3)	5.0(2)
P(3)	0.4655(1)	-0.0709(1)	0.25932(6)	2.63(3)	C(36)	0.7624(6)	-0.3315(6)	0.1134(4)	5.7(2)
P(4)	0.4119(1)	0.2979(1)	0.26127(7)	2.83(3)	C(37)	0.7561(6)	-0.3411(5)	0.1779(4)	5.1(2)
C(1)	0.2533(4)	0.3776(4)	0.3013(3)	3.2(1)	C(38)	0.6658(5)	-0.2639(5)	0.2224(3)	4.0(1)
C(2)	0.3203(4)	-0.1029(4)	0.2711(3)	2.9(1)	C(39)	0.4556(4)	0.3844(4)	0.1986(3)	3.0(1)
C(3)	0.1448(5)	0.4334(4)	0.1915(3)	3.6(1)	C(40)	0.4675(5)	0.4834(5)	0.2162(3)	4.5(1)
C(4)	0.1930(7)	0.3809(6)	0.1310(3)	6.0(2)	C(41)	0.4984(6)	0.5515(5)	0.1674(4)	5.6(2)
C(5)	0.2007(8)	0.4429(7)	0.0766(4)	7.9(2)	C(42)	0.5201(6)	0.5222(5)	0.1036(4)	5.3(2)
C(6)	0.1631(8)	0.5567(7)	0.0844(4)	8.9(2)	C(43)	0.5062(7)	0.4234(6)	0.0865(3)	5.8(2)
C(7)	0.1168(8)	0.6069(6)	0.1437(5)	8.4(3)	C(44)	0.4751(6)	0.3544(5)	0.1342(3)	4.5(2)
C(8)	0.1077(7)	0.5471(6)	0.1983(4)	6.3(2)	C(45)	0.5041(4)	0.2991(4)	0.3192(3)	3.4(1)
C(9)	-0.0120(5)	0.4355(4)	0.3154(3)	4.1(1)	C(46)	0.4586(5)	0.3582(5)	0.3783(3)	3.9(1)
C(10)	-0.0235(7)	0.5022(6)	0.3686(4)	6.3(2)	C(47)	0.5357(6)	0.3534(6)	0.4217(3)	5.1(2)
C(11)	-0.1440(8)	0.5570(7)	0.4049(5)	9.4(3)	C(48)	0.6571(6)	0.2852(6)	0.4048(3)	5.8(2)
C(12)	-0.2420(7)	0.5483(7)	0.3868(5)	8.4(3)	C(49)	0.7023(6)	0.2272(7)	0.3446(4)	6.4(2)
C(13)	-0.2303(6)	0.4839(6)	0.3345(5)	6.9(2)	C(50)	0.6266(5)	0.2323(6)	0.3030(3)	4.9(2)
C(14)	-0.1157(5)	0.4277(5)	0.2973(4)	5.1(2)	C(51)	0.0627(5)	0.1980(4)	0.1851(3)	3.3(1)
C(15)	0.0773(4)	-0.0740(4)	0.2551(3)	3.3(1)	C(52)	0.0079(5)	0.2105(5)	0.1429(3)	3.8(1)
C(16)	0.0742(5)	-0.1478(5)	0.3023(3)	4.8(1)	C(53)	-0.0562(5)	0.2294(7)	0.0890(3)	6.2(2)
C(17)	-0.0211(6)	-0.1909(6)	0.3184(4)	6.2(2)	C(54)	0.0329(9)	0.2324(8)	0.0253(5)	9.4(3)*
C(18)	-0.1130(6)	-0.1606(6)	0.2856(5)	7.0(2)	C(55)	-0.177(1)	0.306(1)	0.1045(7)	14.2(5)*
C(19)	-0.1124(6)	-0.0871(6)	0.2386(5)	7.1(2)	C(56)	-0.080(1)	0.113(1)	0.0748(7)	12.8(4)*
C(20)	-0.0173(5)	-0.0432(5)	0.2231(4)	5.7(2)	C(57)	0.2966(4)	0.1326(4)	0.3146(2)	2.8(1)
C(21)	0.2628(4)	-0.0598(4)	0.1458(3)	3.3(1)	C(58)	0.2059(4)	0.1409(4)	0.3565(2)	2.9(1)
C(22)	0.3002(5)	0.0097(5)	0.1017(3)	4.3(1)	C(59)	0.1185(5)	0.1461(5)	0.4192(3)	3.7(1)
C(23)	0.3470(7)	-0.0275(6)	0.0368(3)	5.9(2)	C(60)	0.1720(7)	0.0399(7)	0.4554(4)	6.6(2)*
C(24)	0.3543(7)	-0.1316(7)	0.0177(3)	6.7(2)	C(61)	0.1088(7)	0.2485(7)	0.4601(4)	6.6(2)*
C(25)	0.3191(7)	-0.2011(6)	0.0615(4)	6.2(2)	C(62)	-0.0088(8)	0.1519(7)	0.4079(4)	7.3(2)*
C(26)	0.2748(6)	-0.1649(5)	0.1249(3)	5.0(2)	Cl(2)	0.7440(2)	0.3491(1)	0.58689(8)	5.60(4)
C(27)	0.5068(5)	-0.0985(4)	0.3369(3)	3.4(1)	O(1)	0.8062(6)	0.2354(4)	0.5690(3)	8.0(2)
C(28)	0.5746(5)	-0.0395(6)	0.3574(3)	4.9(2)	O(2)	0.6911(8)	0.3613(6)	0.6532(3)	12.2(3)
C(29)	0.6064(6)	-0.0622(7)	0.4165(4)	6.8(2)	O(3)	0.6529(7)	0.3893(6)	0.5525(3)	13.5(2)
C(30)	0.5721(7)	-0.1388(7)	0.4547(3)	7.0(2)	O(4)	0.8195(7)	0.4133(6)	0.5754(5)	14.6(3)

^a $B_{eq} = 1/3 \sum_i \sum_j B_{ij} (a_i^* a_j^*) a_i a_j$. Starred entries refer to atoms refined isotropically.

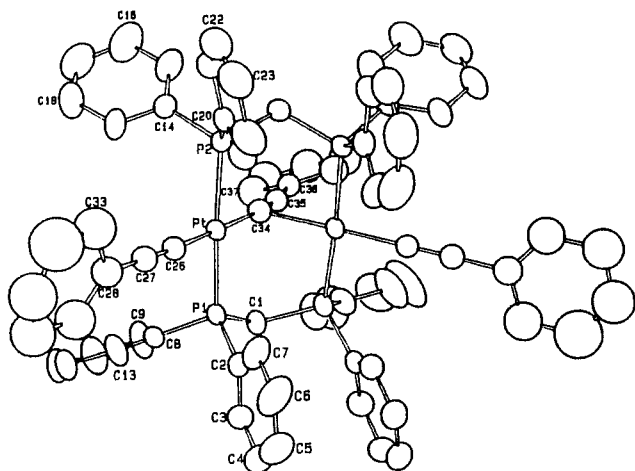


Figure 1. Perspective drawing of the cation of 1 with the atomic numbering.

P(1)—Pt—P(2) (176.22(6)°) and C(26)—Pt—C(34) (178.4(2)°) are close to rectilinear geometry, with P—Pt—C angles close to 90°. The square-planar coordination geometry about each metal center therefore results in an A-frame type of structure, with the methylene linkages of the dpmm groups folded toward the apex of the A-frame, as is commonly observed in these systems.^{4a,13} The Pt—C(26)—C(27) and C(26)—C(27)—C(28) angles of close to 180°, together with the C(26)—C(27) distance of

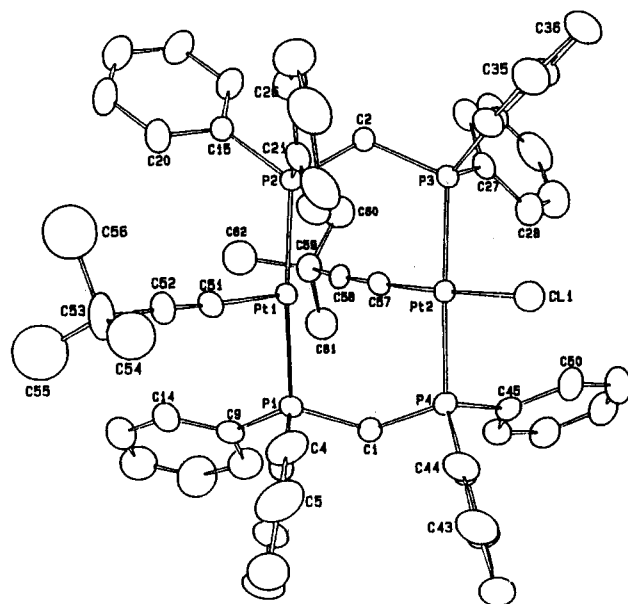


Figure 2. Perspective drawing of the cation of 2 with the atomic numbering.

1.18(1) Å, are indicative of terminal C≡C bonds. Similarly, in 2 the Pt—C(51)—C(52) and C(51)—C(52)—C(53) angles are close to 180° and the C(51)—C(52) distance is 1.194(9) Å. The C—C distances for C(34)—C(35) in 1 and C(57)—C(58) in 2 1.11(1) and 1.209(6) Å, respectively, which seem to be not much different from the accepted values for uncoordinated acetylenes (1.18–1.21 Å).¹⁴ Moreover, the deviations from linearity of the η²-bridging

(13) For examples, see: (a) Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* 1984, 1815. (b) Cowie, M.; Southern, T. G. *Inorg. Chem.* 1982, 21, 246.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 1

Pt...Pt	3.236(1)	P(1)–C(1)	1.827(8)
Pt–P(1)	2.310(2)	P(2') ^a –C(1)	1.834(6)
Pt–P(2)	2.304(2)	C(26)–C(27)	1.18(1)
Pt–C(26)	1.961(7)	C(34)–C(35)	1.11(1)
Pt–C(34)	2.096(5)		
P(1)–Pt–P(2)	176.22(6)	P(1)–C(1)–P(2') ^a	116.4(4)
P(1)–Pt–C(26)	91.6(1)	Pt–C(26)–C(27)	176.5(7)
P(1)–Pt–C(34)	89.12(5)	C(26)–C(27)–C(28)	178.8(6)
P(2)–Pt–C(26)	91.8(1)	Pt–C(34)–C(35)	171.7(9)
P(2)–Pt–C(34)	87.49(5)	C(34)–C(35)–C(36)	171(1)
C(26)–Pt–C(34)	178.4(2)		

^a Symmetry code: $-x, y, 1/2 - z$.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 2

Pt...Pt	3.151(1)	Pt(2)–C(57)	1.970(4)
Pt(1)–P(1)	2.314(1)	P(1)–C(1)	1.836(6)
Pt(1)–P(2)	2.311(1)	P(2)–C(2)	1.835(6)
Pt(1)–C(51)	1.971(6)	P(3)–C(2)	1.848(6)
Pt(2)–Cl(1)	2.326(1)	P(4)–C(1)	1.838(4)
Pt(2)–P(3)	2.298(1)	C(51)–C(52)	1.194(9)
Pt(2)–P(4)	2.312(1)	C(57)–C(58)	1.209(6)
P(1)–Pt(1)–P(2)	172.48(4)	P(3)–Pt(2)–P(4)	162.35(5)
P(1)–Pt(1)–C(51)	91.3(2)	P(3)–Pt(2)–C(57)	82.0(1)
P(2)–Pt(1)–C(51)	88.4(2)	P(4)–Pt(2)–C(57)	86.5(2)
Cl(1)–Pt(2)–P(3)	95.75(5)	P(1)–C(1)–P(4)	114.8(3)
Cl(1)–Pt(2)–P(4)	95.90(5)	P(2)–C(2)–P(3)	117.0(3)
Cl(1)–Pt(2)–C(57)	177.6(2)	Pt(1)–C(51)–C(52)	177.3(4)
C(57)–C(58)–C(59)	164.5(6)	Pt(2)–C(57)–C(58)	176.4(5)

acetylide groups toward *cis*-bent configuration are small (1, C(34)–C(35)–C(36) 9(1)°; 2, C(57)–C(58)–C(59) 15.5(6)°), indicating that the π interactions between the bridging acetylide groups and the second platinum atom are weak. An interesting feature worth mentioning is that in 2, the η^2 -bridging acetylene carbon atom C(57) is closer to the σ -bonded Pt(2) atom than to Pt(1) (Pt(1)–C(57) = 2.245 Å; Pt(2)–C(57) = 1.970(4) Å). It is also not obvious why the *tert*-butylacetylide group, rather than the chloride, bridges the metal centers in 2. Similar observations have also been reported by Shaw and co-workers on [ClPt(μ -dppm)₂(σ, η^2 -C≡CMe)Rh(CO)]PF₆.^{4a}

Photophysical Studies. The electronic absorption spectra of 1 and 2 in acetonitrile exhibit a low energy absorption band centered at ca. 393 (ϵ 16 980 dm³ mol⁻¹ cm⁻¹) and 357 nm (ϵ 9430 dm³ mol⁻¹ cm⁻¹), respectively (Figure 3). The related monomeric [Pt(dppm-*P*)₂(C≡C-Ph)₂] complex shows an absorption band at ca. 345 nm (ϵ_{max} = 19 800 dm³ mol⁻¹ cm⁻¹), which was assigned to be metal-to-ligand [d(Pt) → π^* (PhC≡C-)] charge transfer in nature.^{10,15} With reference to previous spectroscopic work on binuclear d⁸-d⁸ systems, the intense 393-nm band in 1, which is absent in the monomeric counterpart, and the 357-nm band in 2 are most likely derived from a spin-allowed transition resulting from a weak Pt...Pt interaction.^{1a-c} However, the involvement of the acetylide moieties in these transitions should not be overlooked. It is likely that the LUMO is not a pure metal p_σ orbital arising from 6p_z-6p_z interaction but contains substantial π^* (acetylide) character.^{1d} Therefore we favor the assignment as a MMLCT (metal-metal-bond-to-ligand charge transfer) [d σ → p σ / π^*] transition. Similar assignments

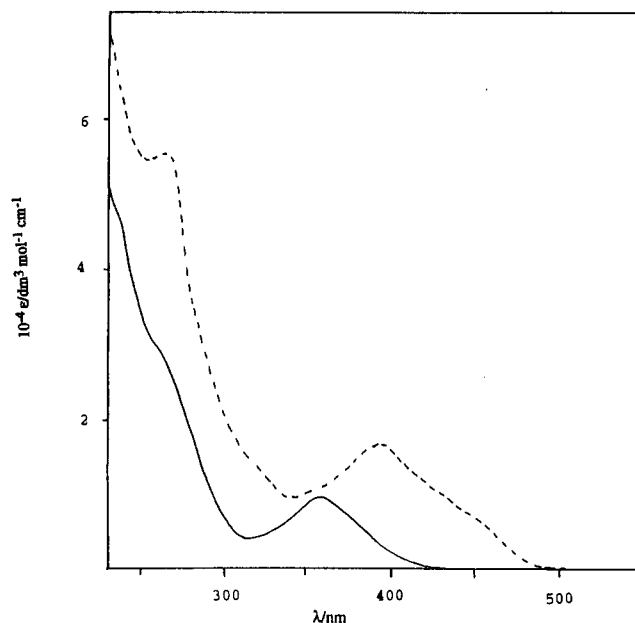


Figure 3. Electronic absorption spectra of 1 (---) and 2 (—) in acetonitrile at room temperature.

Table VI. Photophysical Data for Compounds 1 and 2

compd	medium (temp/K)	λ_{em} /nm ($\tau_0/\mu\text{s}$)
[1]ClO ₄	solid state (298)	618 (2.2 ± 0.2)
	solid state (77)	621
	MeCN (298)	614 (0.11 ± 0.01) ^a
	MeCN (298)	453, 618 ^b
	CH ₂ Cl ₂ (298)	623
[1]Cl	solid state (298)	623 (4.7 ± 0.5)
	solid state (77)	616
	MeCN (298)	618 (0.10 ± 0.01) ^a
	CH ₂ Cl ₂ (298)	625
	EtOH/MeOH (4:1) (298)	618
[2]ClO ₄	EtOH/MeOH (4:1) (77)	589, 665
	solid state (298)	621 (3.5 ± 0.3)
	solid state (77)	624
	MeCN (298)	413, 550–600 (sh)

^a [Pt₂] concentration = 0.22 mM. ^b Under nondegassed condition.

have also been suggested for [Rh₂(dppm)₂(CNR)₄]²⁺ 1⁵ and the dinuclear Pt μ -alkenyldiene complexes.^{1d} The preference for a large π^* (acetylide) character in the LUMO is further supported not only by the blue shift from 1 to 2, which correlates well with the π^* energies of the PhC≡C- and ^tBuC≡C- groups, but also by the relatively small dependence of transition energies on the Pt...Pt distances in 1 and 2. The assignment of a pure d σ → p σ transition is further disfavored on the grounds that a red shift in absorption energies is not observable upon reducing the Pt...Pt separation from 1 to 2. Thus one could alternatively see the transition as having large metal-to-ligand charge transfer character with slight perturbation from weak metal-metal interaction.

Excitation of solid samples of 1 and 2 at $\lambda > 350$ nm at room temperature and at 77 K results in intense orange emission (1, τ_0 (298 K) = 2.2 μs ; 2, τ_0 (298 K) = 3.5 μs). A summary of the photophysical data is collected in Table VI. The solid-state emission spectra of 1 and 2 are depicted in Figure 4. The large Stokes shifts together with the observed lifetimes suggest that the emissive states are likely to be derived from the triplet states. The excitation spectra of 1 and 2 display excitation maxima at ca. 470 and 410 nm, respectively. It is likely that the excitation bands at

(14) Nast, R. *Coord. Chem. Rev.* 1982, 47, 89.

(15) (a) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1971, 44, 2226. (b) Sacksteder, L.; Barait, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* 1991, 30, 2468. (c) Collamati, I.; Furlani, A. *J. Organomet. Chem.* 1969, 17, 457.

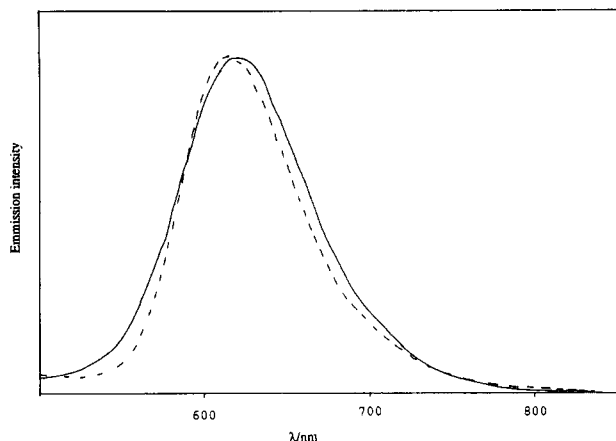


Figure 4. Solid-state emission spectra of 1 (---) and 2 (—) at room temperature.

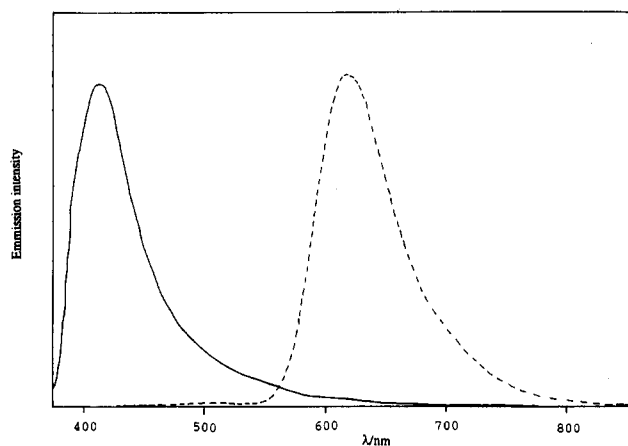


Figure 5. Emission spectra of 1 (---) and 2 (—) in degassed acetonitrile at room temperature.

ca. 470 nm in 1 and 410 nm in 2 are derived from the spin-forbidden MMLCT transition. Excitation of 1 and 2 in fluid solutions at $\lambda > 350$ nm at room temperature also results in long-lived luminescence (Figure 5). The emission spectrum of 1 in degassed acetonitrile exhibits an emission maximum at ca. 614 nm ($\tau_0 = 0.11 \mu\text{s}$; $\phi = 1 \times 10^{-3}$), with a broad excitation maximum found in the 400–500-nm region. The emission spectrum of 2 in

degassed acetonitrile, on the other hand, displays an intense maximum at ca. 413 nm with a very weak shoulder at ca. 550–600 nm. The higher energy 413-nm emission band is assigned as fluorescence, while the shoulder at ca. 550–600 nm is likely derived from phosphorescence. This is supported by the observation that the emission spectrum of 1 in nondegassed acetonitrile showed a weak emission band at 453 nm in addition to the intense band at 618 nm. It is likely that the 453-nm band has been masked by the intense unquenched phosphorescence at 618 nm under degassed conditions. Furthermore, the excitation spectrum of 2 monitored at the 413-nm emission in degassed acetonitrile shows an excitation maximum at ca. 365 nm, corresponding to the spin-allowed MMLCT transition. Similar assignments have also been made for other d^8 – d^8 systems.¹

The phosphorescent state of 1 has been found to be quenched by electron acceptors such as 4-cyano-*N*-methylpyridinium hexafluorophosphate in acetonitrile ($0.1 \text{ mol dm}^{-3} \text{ NBU}_4\text{PF}_6$) at a bimolecular rate constant, k_q , of $2.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Cyclic voltammetric studies of 1 show an irreversible reduction couple at E_{pc} of ca. -1.78 V , a quasi-reversible oxidation couple at ca. $+0.99 \text{ V}$, and an irreversible oxidation couple at E_{pa} of ca. $+1.34 \text{ V}$ vs ferrocene-ferrocenium in MeCN ($0.1 \text{ mol dm}^{-3} \text{ NBU}_4\text{PF}_6$). Assuming the first oxidation couple and the reduction couple to be metal-centered in nature, excited state reduction potentials $E_f[\text{Pt}_2(2+/+*)]$ of $< -0.47 \text{ V}$ and $E_f[\text{Pt}_2(+*/0)]$ of $> 0.96 \text{ V}$ vs NHE are estimated for 1 [$E_{0-0} \approx 2.1 \text{ eV}$].

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Supplementary Material Available: Lists of hydrogen atom coordinates (1, Table SI; 2, Table SVI), general displacement parameter expressions, U (1, Table SII; 2, Table SVII), complete bond distances (1, Table SIII; 2, Table SVIII), and complete bond angles (1, Table SIV; 2, Table SIX) (9 pages). Ordering information is given on any current masthead page.

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