(1.390 Å), and the P(2)–N(1) and P(3)–N(3) distances (mean 1.728 Å) are longer than the inner P(2)–N(2) and P(3)–N(2) distances (mean 1.701 Å). The P(2)–N(1) and P(3)–N(3) bonds are relatively long for typical phosphazane P–N bonds (eg. 1.65–1.70 Å)[1,2,4c,e] however, the other P–N distances in **3b** are as expected.

The tetraphosphazanes **1**–**4** are characterized by a combination of ^{1}H and ^{31}P NMR, IR, and mass spectral data. All show basic AA′XX′ or AA′BB′ ^{31}P NMR spectral patterns,[12] analogous to that of **3b** and consistent with the presence of only one isomer. Hence all series members are inferred to be structurally analogous to **3b**, i.e. trans bonded around the central P(2)–N(2)–P(3) linkage. The $^2J_{P(2)P(3)}$ coupling constant of 70.4 Hz in **1** is consistent with those seen in *trans*-diphosphinoamines reported previously.[13] The outer P–N–P couplings, $^2J_{P(1)P(2)}$ and $^2J_{P(3)P(4)}$, are slightly smaller and assumed to be the average of all possible conformations around the exo P–N bonds. Similar comparison data for the λ^4–λ^3 (**2** or **4**) or the λ^4–λ^4 compound (**3a** and **3b**) are not available; however, it is of interest to note that $^2J_{P(2)P(3)}$ values in **3** and **4** are smaller than that observed in **1**.

Compound **1** is an unique example of a molecule containing a diphosphinoamine unit [P(2)–N(2)–P(3)] stereoselectively formed as the trans *d,l* isomer. Although reaction of $PhPCl_2$ with *i*-$PrNH_2$ yields *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$ diastereomerically selectively,[14] such selectivity has not been recognized generally in diphosphinoamine formation reactions. How formation of **1** as one diastereomer results and is a function of the skeletal stabilization in the system is of interest. Perhaps with substituent modifications, such reactions can be used in other stereoisomeric selective syntheses.

The successful attachment of a tetraphosphazane unit to three adjacent positions on a benzene ring without major distortion of the systems or loss of planarity suggests that it might be possible to extend the phosphazane skeleton to completely encircle the C_6 ring with an $(RPN)_6$ "supercycle" azane ring. Such molecules and their derivatives might have novel magnetic and/or electronic properties analogous to those reported recently by Breslow and co-workers.[15]

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Supplementary Material Available: Listings of the crystal structure determination and crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra of Charge-Transfer Excited States of Copper(I) Complexes

Sir:

Resonance Raman spectroscopy is now well-established[1] as an important probe of the charge-transfer excited states of metal complexes and in particular as an effective way of investigating the extent of localization of the excited electron on acceptor ligand orbitals.[2] With one exception,[3] previous work has focused attention on the excited states of d^6 metal ion complexes. We wish here to report the first examples of resonant Raman scattering from the excited states of some photoelectrochemically interesting[4] d^{10} systems, namely the metal–ligand charge-transfer (MLCT) states of the four-coordinate copper(I) complexes $[Cu(DPP)_2]^+$ and $[Cu(DMP)(Ph_3P)_2]^+$ (DPP and DMP are respectively 2,9-diphenyl- and 2,9-dimethyl-1,10-phenanthroline), for which we have recently measured[5] excited-state absorption spectra. The results provide convincing evidence that in the MLCT excited state of $[Cu(DPP)_2]^+$, the transferred electron is localized on one ligand. Our findings suggest that localized excitation, originally demonstrated for the CT excited states of a variety of Ru(II) complexes,[2] is a rather general phenomenon among the MLCT excited states of transition-metal systems.

The resonance Raman studies were carried out at the Laser Support Facility of the U.K. Science and Engineering Research Council (Rutherford Appleton Laboratory). Ground-state spectra were generated by means of an Ar$^+$ laser (Innova 90) at wavelengths of 363.8 and 488 nm. An excimer-pumped dye laser (Lambda Physik FL2002E) was used for the excited-state investigations. In all cases, the excited-state lifetimes were sufficiently long in comparison with the laser pulse duration (10 ns) and the extent of overlap of the ground- and excited-state absorption spectra of the complexes was such that the same laser pulse served both to populate and to interrogate the excited species. The complexes were prepared by literature methods.[4b,c] Argon-purged solutions in methanol (ca. 10^{-3} mol dm^{-3}) were flowed through quartz capillary sample tubes, and the laser beam was brought to a focus just beyond the irradiated zone. Raman scattered radiation, dispersed through a Spex Triplemate spectrograph (1200 lines/mm grating), was detected by an intensified diode array (EG&G, Model 1420). Raman spectra of indene and cyclohexane, recorded under the same experimental conditions as the complex spectra, were used for calibration purposes. Spectra recorded on several different visits to the Laser Centre were very reproducible, and the peak positions in the spectra reported here are reliable to better than 4 cm^{-1}.

As a strategy for establishing the nature of the MLCT excited states of the bis(ligand) complex, resonance Raman spectra of $[Cu(DPP)_2]^+$ were compared with those of the mixed-ligand species $[Cu(DMP)(Ph_3P)_2]^+$. The latter complex has[4c] an intense MLCT (Cu→DMP) band in the region of 360 nm, and the charge-transfer state populated by excitation in this spectral region necessarily has the excited electron localized on the single DMP ligand. The photoexcited complex is thus in effect a source of the disubstituted 1,10-phenanthroline radical anion.[6] Figure 1a shows the excited-state absorption spectrum, with UV and visible bands resembling the published[7] absorption spectra of the radical anions of 1,10-phenanthroline and related N-heteroaromatic

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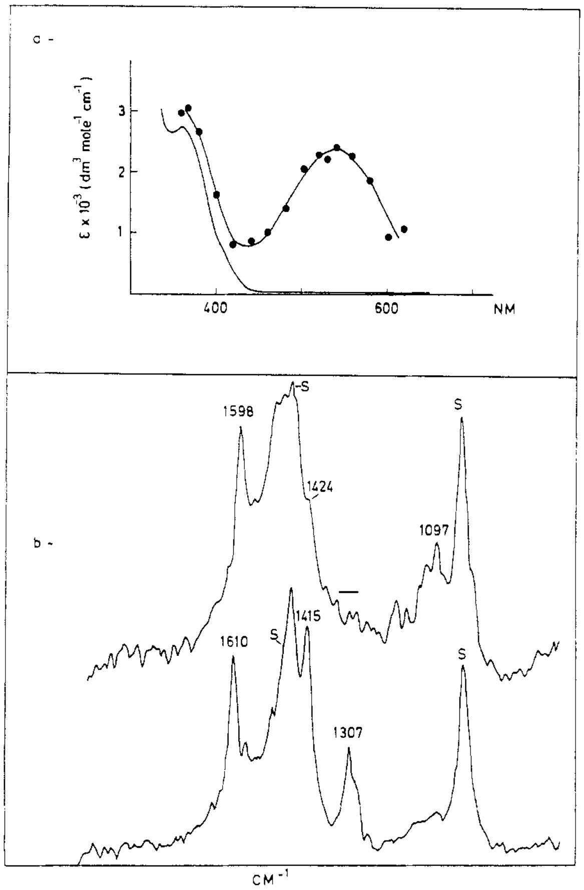

Figure 1. (a) Excited-state (●) and ground-state (–) absorption spectra of [Cu(DMP)(Ph$_3$P)$_2$]BF$_4$ in MeOH. The excited-state spectrum was recorded point-by-point following excitation at 354.7 nm by using the Q-switched Nd^{3+}/YAG laser described in ref 5a. (b) Resonance Raman spectra of argon-purged solutions of [Cu(DMP)(Ph$_3$P)$_2$]BF$_4$, 10^{-3} mol dm^{-3} in MeOH: lower trace, ground-electronic-state spectrum recorded with CW excitation (50 mW, Ar$^+$ laser) at 363.8 nm; Upper trace, excited-state spectrum recorded with a pulsed dye laser (2.5 mJ pulse energy) at 360 nm. Positions of peaks are given in wavenumbers with solvent scattering marked S.

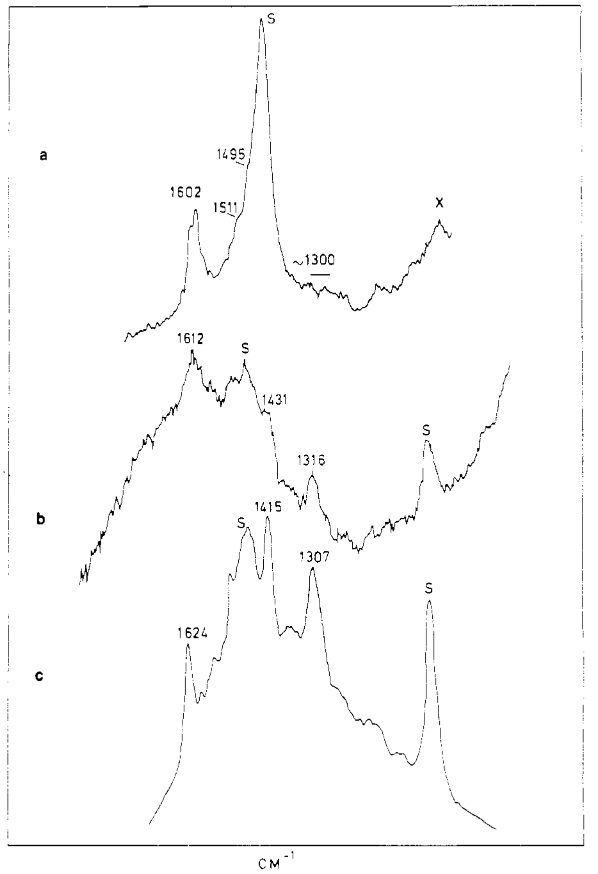

Figure 2. Resonance Raman spectra of argon-purged solutions of [Cu(DPP)$_2$]ClO$_4$, ca. 10^{-3} mol dm^{-3} in MeOH: (a) Excited state spectrum recorded with a pulsed dye laser (5 mJ pulse energy) at 540 nm; (b) excited-state spectrum recorded with a pulsed dye laser (4 mJ pulse energy) at 360 nm; (c) ground-electronic-state spectrum recorded with CW excitation (100 mW, Ar$^+$ laser) at 363.8 nm. The wavenumber scales used in parts a–c are not the same. In each spectrum, the actual positions of peaks are indicated in wavenumbers, with solvent scattering denoted by S. The feature marked X in spectrum a is an artifact, arising from proximity to one edge of the intensified segment of the diode array.

hydrocarbons. The MLCT excited state of the bis(ligand) complex, [Cu(DPP)$_2$]$^+$, also absorbs[5a] in the visible region with a band of intensity at 540 nm (ϵ_{540} ca. 2800 dm^3 mol^{-1} cm^{-1}) comparable to that in Figure 1a but much broader due to overlap with intense UV absorptions (ϵ_{360} ca. 9000 dm^3 mol^{-1} cm^{-1}.)

The ground-state resonance Raman spectrum of the mixed-ligand complex excited at 363.8 nm is shown in the lower trace of Figure 1b. The upper trace shows the corresponding spectrum of the excited state, populated and "simultaneously" probed at 360 nm by a dye laser pulse of short duration (10 ns) in comparison with the excited-state lifetime[4c,5b] (ca. 300 ns at room temperature in methanol). At the typical pulse energies used (2.5 mJ), there is a significant excess of laser photons over molecules of complex in the irradiated zone (volume ~ 0.5 mm^3) so that the ground state is bleached. The Raman spectrum is therefore predominantly due to excited-state scattering resonantly enhanced through the 360-nm absorption band, which is assigned to a DMP ligand radical-anion-centered transition, as is also the band at 540 nm. While shifts are observed in the positions of several of the Raman peaks, the striking difference between the two spectra is the loss in the excited-state spectrum of the band at 1307 cm^{-1} characteristic of neutral ligand. The disappearance of this 1300-cm^{-1} feature thus serves as a convenient spectroscopic marker for the conversion of neutral ligand to radical anion. [Under equivalent conditions at the same excitation wavelength, the resonance Raman spectrum of the complex with the unsubstituted 1,10-phenanthroline ligand, [Cu(phen)(Ph$_3$P)$_2$]$^+$, does show a neutral ligand mode at 1304 cm^{-1}.] The excited-state lifetime in this case ($\leq$1 ns in methanol at room temperature) is short compared to the excitation laser pulse duration, and thus the principal contribution to the Raman scattering is from the ground electronic state.

Resonance Raman spectra of the bis(ligand) complex, [Cu(DPP)$_2$]$^+$, are shown in Figure 2. The ground-state spectrum excited at 363.8 nm (Ar$^+$ laser) and that of the excited state populated and probed at 360 nm (dye laser) are compared in parts b and c, while part a displays the excited-state spectrum generated at a different dye laser excitation wavelength (540 nm). The same thermally equilibrated excited state is populated at both these wavelengths, as shown[5a] by the invariance of the excited-state lifetimes with laser excitation wavelength. The 540-nm resonance-enhanced spectrum, although dominated by an intense solvent band, shows features at 1602, 1511, and 1495 cm^{-1}, all of which must be due to excited-state scattering since the ground state is effectively bleached by the "pump + probe" laser pulse. The significant feature here is the total absence of peaks in the 1300-cm^{-1} region.[8] We therefore conclude that the spectrum in Figure 2a is attributable to vibrational modes of the DPP$^{\bullet-}$ radical anion; thus, the excited-state absorption at 540 nm responsible for the resonance enhancement is assigned to a radical anion-centered $\pi \rightarrow \pi^*$ transition.

In contrast to the situation at 540 nm, the excited-state resonance Raman spectrum generated at 360 nm (Figure 2b) does

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(8) Under identical pulse excitation conditions at this wavelength, the bis(ligand) complex, [Cu(DMP)$_2$]$^+$ (which has a much shorter-lived and hence under our conditions non-saturated excited state), does exhibit neutral ligand peaks in this region, due to ground-state scattering.

show a relatively strong band at 1316 cm^{-1}, characteristic of neutral DPP ligand. Although the signal:noise ratio is lower,[9] the spectrum obviously resembles that of the ground-state, but under the saturation conditions that prevail, the scattering cannot arise from the ground state and must therefore be attributed to vibrational modes of the neutral ligand, in the MLCT excited state of the complex. The resonance enhancement here is principally ascribed to a LMCT transition (from neutral DPP ligand to the formal[4a] Cu^{II} center), which in this bis(ligand) complex is the probable major source of the excited-state absorption in the 360-nm region.

By selective excitation in different absorption bands of the MLCT excited state of $[Cu(DPP)_2]^+$ we have therefore been able to observe resonantly enhanced Raman features characteristic of either the neutral DPP ligand or the radical anion. This provides convincing evidence for a localized formulation of the excited state: $[Cu^{II}(L)(L^{\bullet-})]^+$, on the 10-ns timescale of the present experiments. The results, which are the first of this type reported for the excited states of d^{10} transition-metal complexes, are a further example of the potential of resonance Raman spectroscopy for the investigation of charge-transfer excited states. Furthermore, the ability of the technique, demonstrated in the present work and elsewhere,[1,2,10] to selectively monitor both "neutral" and electron-rich or electron-deficient regions of molecules suggests its wider application as a structural probe of photogenerated, charge-*separated* species[11] in the study of the factors controlling electron-transfer rates in such systems.

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Correlation between ^{119}Sn Isomer Shifts and Quadrupole Coupling Constants for Dimethyltin(IV) Salts of Strong Protonic Acids and Superacids

Sir:

For a series of dimethyltin(IV) derivatives of very strong protonic acids and superacids, a linear correlation between the ^{119}Sn isomer shift δ (relative to SnO_2) and the quadrupole coupling constant ΔE_Q is noted. The resulting order, apparent from a δ vs. ΔE_Q plot, allows an estimation of relative basicity in the solid state for the corresponding acid and superacid anions present in these $(CH_3)_2Sn$ derivatives. The purpose of this communication is (a) to identify the structural and spectroscopic features of dimethyltin(IV) salts, allowing a correlation, (b) to provide a rationale for such a correlation between δ and ΔE_Q, and (c) to suggest the use of the $(CH_3)_2Sn$ group as an electronic probe in the estimation of anion basicities, which may hopefully also be applicable to strongly acidic and superacidic systems.

Table I. ^{119}Sn Mössbauer Data of Dimethyltin(IV) Derivatives of Strong Protonic Acids and Superacids at 77 K

no.[d]	compd	ΔE_Q,[a] mm s^{-1}	δ,[a,b] mm s^{-1}	ref
1	$(CH_3)_2SnF_2$	4.52	1.23	1
2	$Li_2[(CH_3)_2SnF_4]$	4.60	1.31	*c*
3	$(CH_3)_2Sn(SO_3\text{-}p\text{-}CH_3C_6H_4)_2$	4.85	1.51	5
	$(CH_3)_2Sn(SO_3C_2H_5)_2$	4.91	1.55	5
4	$(CH_3)_2Sn(SO_3CH_3)_2$	5.05	1.52	5
5	$(CH_3)_2Sn(PO_2F_2)_2$	5.13	1.53	4
6	$(CH_3)_2Sn(SO_3Cl)_2$	5.20	1.75	5
7	$(CH_3)_2Sn(TaF_6)_2$	5.23	1.69	11
	$Ba[(CH_3)_2Sn(SO_3F)_4]$	5.37	1.76	10
8	$Cs_2[(CH_3)_2Sn(SO_3CF_3)_4]$	5.39	1.74	9
	$Cs[(CH_3)_2Sn(SO_3F)_3]$	5.39	1.80	10
	$Li_2[(CH_3)_2Sn(SO_3F)_4]$	5.42	1.77	10
9	$Cs_2[(CH_3)_2Sn(SO_3F)_4]$	5.50	1.83	9
10	$(CH_3)_2Sn(NbF_6)_2$	5.51	1.77	11
	$(CH_3)_2Sn(SO_3CF_3)_2$	5.51	1.79	5
11	$(CH_3)_2Sn(SO_3F)_2$	5.55	1.80	5
12	$(CH_3)_2Sn[Pt(SO_3F)_6]$	5.67	1.95	9
13	$[(CH_3)_2SnSO_3F]_2[Pt(SO_3F)_6]$	5.70	1.96	9
14	$(CH_3)_2Sn(Sb_2F_{11})_2$	6.01	2.08	11
	$(CH_3)_2Sn(SbF_6)_2$	6.04	2.04	11

[a] Confidence limit ±0.03 mm s^{-1}. [b] Relative to SnO_2 at 77 K. [c] Karunanithy, S.; Aubke, F.; Sams, J. R., to be submitted for publication. [d] Numbers in column 1, refer to data and numbers used in Figure 1.

Solvolysis of either $(CH_3)_4Sn$, $(CH_3)_3SnCl$, or $(CH_3)_2SnCl_2$ in strong protonic acids such as HF, HPO_2F_2, or the sulfonic acids HSO_3X with X = F, Cl, CF_3, $p\text{-}CH_3C_6H_4$, CH_3, or C_2H_5 is a convenient route to dimethyltin(IV) derivatives of these acids.[1–6] Structures reported for two of the resulting compounds, $(CH_3)_2SnF_2$[7] and $(CH_3)_2Sn(SO_3F)_2$,[8] reveal essentially linear C–Sn–C groups with octahedral coordination for tin achieved by weakly coordinated, symmetrically bridging bidentate F or SO_3F anions. A similar geometry for tin in all dimethyltin(IV) salts of these strong acids is indicated by their ^{119}Sn Mössbauer spectra. Most evident here are the unusually large quadrupole coupling constants, which range from 4.50 to 5.50 mm s^{-1} and rank among the highest so far reported for tin. Some novel derivatives of these dimethyltin(IV) salts have very recently been synthesized by us[9–11] and their ^{119}Sn Mössbauer spectra exhibit similar, high quadrupole coupling constants. These include anionic derivatives of the types $[(CH_3)_2Sn(SO_3F)_3]^-$ and $[(CH_3)_2Sn(SO_3X)_4]^{2-}$ with X = F or CF_3, which have ΔE_Q values of ~5.4–5.5 mm s^{-1},[9,10] while cationic derivatives with either $[(CH_3)_2Sn(SO_3F)]^+$ or $(CH_3)_2Sn^{2+}$, stabilized by anions like $[M(SO_3F)_6]^{2-}$, with M = Sn or Pt,[9] or by SnF_6^{2-},[11] show ΔE_Q values between 5.50 and 5.70 mm s^{-1}. Finally, for dimethyltin(IV) salts with either $Sb_2F_{11}^-$ or SbF_6^- as counteranions, exceptionally high quadrupole coupling constants of ~6.0 mm s^{-1} are observed.[11] These cationic salts and their TaF_6^- and NbF_6^- analogues may be viewed as derived from superacids such as HF–SbF_5 or HSO_3F–$Pt(SO_3F)_4$.[12]

The ^{119}Sn Mössbauer parameters for all these $(CH_3)_2Sn$ derivatives are listed in Table I in order of increasing ΔE_Q values. A few additional examples in this series, those with two different tin environments, as e.g. $(CH_3)_2Sn[SnF_6]$, are omitted because

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