on the basis of our preliminary kinetic results.

$$\vec{K}_{\mathrm{rel}} = \frac{[\mathrm{UO_2{\cdot}\mathbf{3}}][\mathrm{CO_3}^{2-}]^3}{[\mathrm{UO_2(CO_3)_3}][\mathbf{3}]} = 10^{-1.05}$$

$$\overleftarrow{K}_{\mathrm{rel}} = \frac{[\mathrm{UO_2(CO_3)_3}][\mathbf{3}]}{[\mathrm{UO_2{\cdot}\mathbf{3}}][\mathrm{CO_3}^{2-}]^3} = 10^{0.74}$$

$$K_{\mathrm{rel}}(\mathrm{av}) = \frac{[\mathrm{UO_2{\cdot}\mathbf{3}}][\mathrm{CO_3}^{2-}]^3}{[\mathrm{UO_2(CO_3)_3}][\mathbf{3}]} = 10^{-0.89}$$

$$K = \frac{[\mathrm{UO_2{\cdot}\mathbf{3}}]}{[\mathrm{UO_2}][\mathbf{3}]} = 10^{20.7}$$

In conclusion, very appropriately designed[16] uranophile $\mathbf{3}{\cdot}\mathrm{Na_3}$ forms a stable complex with uranyl ion, which shows characteristic absorption in electronic spectrum, allowing precise equilibrium study. Association constant between uranyl and **3** in water is the largest among those directly measured.[17]

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[16] The diameter of the cavity is ca. 2.1 Å on the basis of the CPK model. Sulfur ligation is known as one of the strongest among those ever studied in the authors' laboratory.

[17] (a) Stronski, I.; Zielin, A.; Samotus, A.; Stasicka, Z.; Budesinsky, B. *Z. Anal. Chem.* **1966**, *222*, 14. Association constant of $10^{24.3}$ $\mathrm{M}^{-1}$ was reported, based on indirect measurements. Our preliminary results show that the association constant is much smaller. (b) Budesinsky, B.; Hass, K.; Bezdekova, A. *Coll. Czech. Chem. Commun.* **1967**, *32*, 1528. Association constant of $10^{(09}$ $\mathrm{M}^{-2}$ was reported but molarity was not carefully determined.

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# Mixed-Metal Atom Cluster Compound Containing Silver(I) and Platinum(II)

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We wish to report the preparation and structural definition of a mixed-metal atom cluster compound that has a number of unusual features. It is the first example, so far as we know, of a compound that contains both silver–silver and silver–platinum bonds.

By reaction of equimolar quantities of $\mathrm{AgNO_3}$ and $\mathrm{(NBu_4)_2}$ [*trans*-$\mathrm{PtCl_2(C_6F_5)_2}$][1] in methanol according to eq 1, a yellow solid

$$2(\mathrm{NBu_4})_2[t\text{-}\mathrm{PtCl_2(C_6F_5)_2}] + 2\mathrm{AgNO_3} \rightarrow 2(\mathrm{NBu_4})\mathrm{NO_3} + (\mathrm{NBu_4})_2[\mathrm{Pt_2Ag_2Cl_4(C_6F_5)_4}] \quad (1)$$

compound, **1**, is precipitated. This compound was first characterized by elemental analysis, conductance, and infrared spectroscopy.[2] At room temperature the solid darkens to pale brown within about 1 month whereas an acetone solution decomposes in a few hours even at −25 °C, depositing AgCl. The other products of decomposition have not yet been identified. This instability made it very difficult to obtain crystals but by slow diffusion of $i\text{-}\mathrm{C_3H_7OH}$ into an acetone solution at −25 °C this was accomplished, and the structure was then solved by X-ray crystallography.[3]

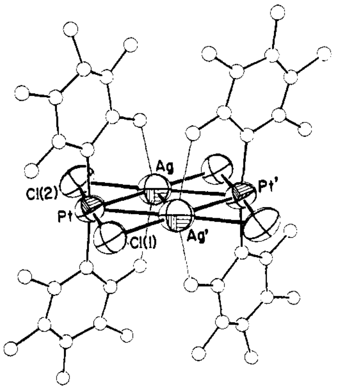

**Figure 1.** ORTEP drawing of the entire $[\mathrm{Pt_2Ag_2Cl_4(C_6F_5)_4}]^{2-}$ ion.

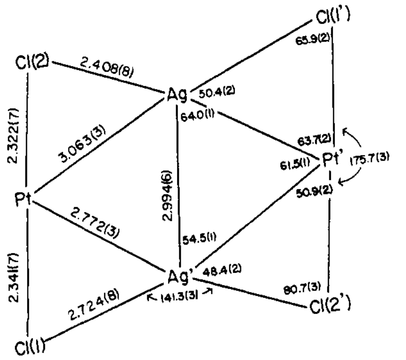

**Figure 2.** Drawing of the central $\mathrm{Ag_2Pt_2Cl_4}$ plane, showing principal bond lengths and angles.

The entire molecular structure is shown in Figure 1 and the central, essentially planar $\mathrm{Ag_2Pt_2Cl_4}$ unit, with principal bond lengths and angles, is shown in Figure 2. The molecule is rigorously centrosymmetric. Considering first the central $\mathrm{Ag_2Pt_2Cl_4}$ unit, we note that the metal atoms would conventionally be assigned oxidation numbers of I and II for Ag and Pt, respectively, and that each Pt atom is linked to an essentially trans-planar set of Cl and C atoms with normal bond lengths: Pt–Cl, 2.322 (7), 2.341 (7) Å; Pt–C, 2.04 (3), 2.07 (3) Å. The two $\mathrm{PtCl_2(C_6F_5)_2}$ units then embrace a central $\mathrm{Ag_2}$ unit in which the Ag–Ag distance is 2.994 (6) Å. Each silver atom then has close contact with one platinum atom, 2.772 (3) Å, which surely represents a Pt–Ag bond of considerable strength as well as a longer contact, 3.063 (3) Å, with the other platinum atom. The strength of Pt–Ag bonding across this longer distance is a moot point. Each Ag atom also has contacts to Cl atoms at distances of 2.408 (8) Å, which represents a strong bonding interaction, and 2.724 (8) Å, which probably indicates some fractional bonding. The Ag–Ag distance is near the high end of the range (vide infra) that is spanned by previous cases in which Ag–Ag bonding has been presumed to occur.

One of the most remarkable features of this structure is the close approach of two ortho fluorine atoms to each Ag atom, at distances of 2.60 (1) and 2.69 (1) Å. The expected length[4] of an Ag–F bond would be 1.98 Å, so that the interaction here does not approach true bond formation, but it would appear that it must contribute to the stability of the cluster, since, otherwise, rotation about the Pt–C bonds could easily lead to an apparent overall lessening of nominally nonbonding contacts.

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[1] Uson, R.; Forniés, J.; Martinez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

[2] Calcd for $\mathrm{C_{56}H_{72}N_2F_{20}Cl_4Ag_2Pt_2}$: C, 35.38; H, 3.79; N, 1.47. Found: C, 35.20; H, 3.73; N, 1.48. Λ (~5 × $10^{-4}$ M in acetone): 218 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$; IR 770 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{C-F}}$), 320 $\mathrm{cm^{-1}}$ (broad, $\nu_{\mathrm{Pt-Cl}}$).

[3] Crystal system: triclinic ($P\bar{1}$ assumed), with $a$ = 12.438 (9) Å, $b$ 13.160 (7) Å, $c$ = 11.129 (8) Å, $\alpha$ = 103.53 (5)°, $\beta$ = 101.27 (6)°, $\gamma$ = 74.75 (5)°, $Z$ = 1. Of 2621 measured reflections, those 1616 unique reflections with $F^2 \geq 3\sigma(F^2)$ were corrected for Lorentz and polarization effects, absorption and anisotropic decay of 45% over 157 h of exposure, and used to solve the structure. Final refinement of 293 variables for 43 atoms (24 refined anisotropically) led to $R$ = 0.079 and $R_w$ = 0.097. A list of atomic positional parameters is available as supplementary material.

[4] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 403.

0002-7863/84/1506-2482$01.50/0

In seeking precedents for the Ag to Pt metal–metal bonding in this molecule, we have found only two very recently reported possibilities. B. L. Shaw et al.[5,6] have reported the preparation and structure of $(PhCC)_2Pt(\mu\text{-dppm})_2AgI$, with a Pt--Ag distance of 3.146 (3) Å, which the authors felt[5] did "not exclude significant bonding interaction". In the case of a trinuclear Pt–Ag–Pt compound the Pt–Ag distances of 2.849 (1) and 2.884 (1) Å were considered by Lippert and Neugebauer[7] to be "too long to implicate any strong metal–metal bonding...However, some weak metal–metal interaction appears feasible on the basis of Pt and Ag radii". Short, and hence potentially bonding, Ag–Ag distances have often been observed, and the range is from 2.740 (2) Å for a compound in which the silver atoms are bridged by a carbon atom of a ferrocene group[8] to distances as high as 2.957 (2)–3.085 (2) Å where an "attractive interaction between the Ag atoms" of an $Ag_8$ cube was proposed[9] and 3.074 (2) Å in a case where the authors neither proposed nor discounted Ag–Ag bonding.[10] The other reported Ag–Ag distances where bonding is considered to occur range from 2.757 to ca. 3.05 Å.[11-19] As further points of comparison, the Ag–Ag distance in metallic silver[20] is 2.889 (6) Å and pertinent sums of Pauling $R_1$ radii[4] are Ag–Ag = 2.68, Pt–Pt = 2.60, and Ag–Pt = 2.64. It may also be noted that the Ag–Rh bonds found in $\{[(\eta\text{-}C_5H_5)(CO)(PPh_3)Rh]_2Ag\}^+$ are 2.651 (1) and 2.630 (1) Å in length.[21]

Studies of the chemical reactivity of this unusual cluster anion are in progress and have revealed, inter alia, that with $PPh_3$ a scission occurs to give a $[PtAgCl_2(C_6F_5)_2PPh_3]^-$ ion in which, according to an as yet incomplete X-ray study, an Ag–Pt bond of length 2.80 Å is retained.

**Acknowledgment.** We thank the U. S. National Science Foundation and the C.A.Y.C.I.T. (Spain) for support.

**Supplementary Material Available:** A table of atomic positional parameters (2 pages). Ordering information is given on any current masthead page.

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(20) Wyckoff, R. W. G. "Crystal Structures", 2nd ed.; Wiley-Interscience: New York, 1963; Vol. 1, p 10. From the unit cell edge, 4.086 Å, the internuclear distance of 2.88 Å is calculated.

(21) Connelly, N. G.; Lucy, A. R.; Galas, A. M. R. *J. Chem. Soc., Chem. Commun.* **1981**, *43*.

# *Additions and Corrections*

**Orthoquinone Complexes of Vanadium and Their Reactions with Molecular Oxygen** [*J. Am. Chem. Soc.* **1983**, *105*, 2680–2686]. Marion E. Cass, David L. Green, Robert M. Buchanan, and Cortlandt G. Pierpont*

Page 2680: The crystallographic unit cell dimensions in the abstract were presented in incorrect order. The cell constants should read as follows: $a$ = 11.633 (4) Å, $\beta$ = 13.102 (4) Å, $c$ = 11.486 (4) Å, $\alpha$ = 108.81 (3)°, $\beta$ = 97.82 (3)°, and $\gamma$ = 100.58 (2)°.

**Selectivities of $\pi$- and $\sigma$-Succinimidyl Radicals in Substitution and Addition Reactions. Appendix: Response to Walling, El-Taliawi, and Zhao** [*J. Am. Chem. Soc.* **1983**, *105*, 5125–5131]. P. S. Skell,* R. L. Tlumak, and S. Seshadri

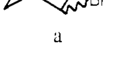
Page 5127, column 2, line 9: $k_{10}/k_7$ = 6.9 should be $k_{11}/k_8$ = 6.9.

**Metacyclophanes and Related Compounds. 6. Reduction of [2.2]Metaparacyclophanequinone** [*J. Am. Chem. Soc.* **1983**, *105*, 6650]. Masashi Tashiro,* Keizo Koya, and Takehiko Yamato

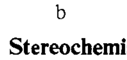
Page 6650: This statement "[2.2]metaparacyclophanequinones have not been synthesized previously" is an error. Earlier, Prof. H. A. Stabb et al. have prepared and characterized [2.2]metaparacyclophanequinone, which is published in *Tetrahedron Lett.* **1979**.

**Solvolyses of $\alpha$-Keto Norbornyl Trifluoroacetates and Triflates. Discrete $\alpha$-Keto Cations vs. $\sigma$-Assisted ($k_\Delta$) Processes** [*J. Am. Chem. Soc.* **1983**, *105*, 7123–7129]. Xavier Creary* and Cristina C. Geiger

Reference to related studies on bromocamphor systems **a** was inadvertently omitted. While our rate and product studies implicated $k_\Delta$ processes in solvolyses of triflates **b**, previous studies on products formed from silver ion promoted reactions of **a** had also implicated $k_\Delta$ processes. See: (a) Bêquê, J. P.; Charpentier-Morize, M.; Pardo, C.; Sansoulet, J. *Tetrahedron* 1978, 293–298. (b) Charpentier-Morize, M. G. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1983**, *28(2)*, 297–318.



a



b

**Photochemical Transformations. 35. Stereochemistry of Electron Transfer from Photoexcited Aromatic Rings to Carbon–Chlorine Bonds. Syn Sterochemistry of Migration in Photo-Wagner-Meerwein Rearrangements** [*J. Am. Chem. Soc.* **1983**, *105*, 7337–7345]. Stanley J. Cristol,* Dave G. Seapy, and Ellen O. Aeling

Page 7343, column 1: In lines 22 and 29 2-(2′,3′-dimethoxybenzoyl)benzoic acid should be 2-(3′,4′-dimethoxybenzoyl)benzoic acid. In lines 28, 35, and 41 2-(2′,3′-dimethoxybenzyl)benzoic acid should be 2-(3′,4′-dimethoxybenzyl)benzoic acid.