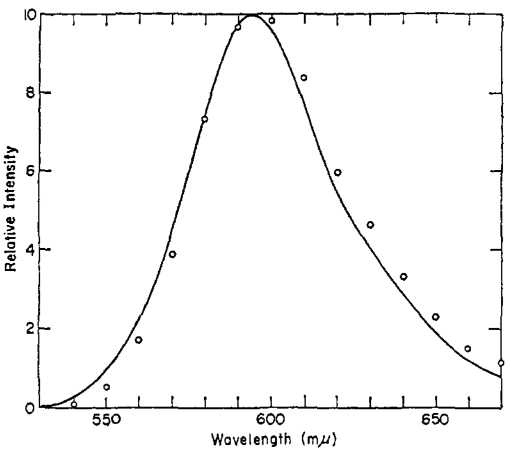

Figure 1. Comparison between chemiluminescence and fluorescence spectra of ruthenium chelates. (———) Fluorescence spectrum of the Ru(bipy)$_3^{+2}$ chelate in aqueous solution; (o-o-o-o) points taken from the chemiluminescence spectrum of the Ru(bipy)$_3^{+3}$ chelate.

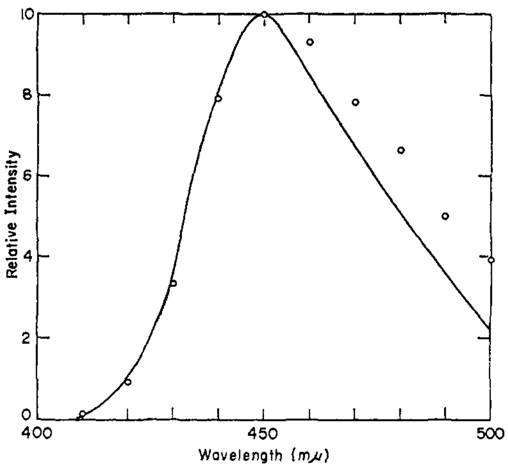

Figure 2. Comparison between the chemiluminescence and fluorescence spectra of 1,6-diaminopyrene. (———) Fluorescence spectrum of 1,6-diaminopyrene in DMF; (o-o-o-o) points taken from the chemiluminescence spectrum of the oxidized diamine.

cence spectrum was obtained on the same spectrofluorometer. Both spectra are unconnected for monochromator–photomultiplier response characteristics (RCA-1P21). It is evident from Figure 1 that the two spectra are identical.

The over-all reaction for the second type system studied can be written as

$$RNH_2^{+m} + \text{reductant} \longrightarrow RNH_2 + h\nu \qquad (2)$$

where RNH$_2$ represents an aromatic amine. The compound used in the present study was 1,6-diaminopyrene. Cyclic voltammetry indicated two reversible waves for 1,6-diaminopyrene, one corresponding to oxidation to the radical cation ($m = 1$) and the other to the dication ($m = 2$). The diamine is also capable of forming stable, solid, radical salts.[9] Electron spin resonance was used to prove the presence of radicals both in solid-state salt preparations and in dimethylformamide (DMF) solution.

Experimentally there are two procedures leading to light emissions for 1,6-diaminopyrene. The first was analogous to the ruthenium system. A DMF solution, millimolar in the diamine, was oxidized with solid lead dioxide or chlorine gas. The lead dioxide was separated by centrifugation or the chlorine was separated by bubbling with nitrogen gas. The resulting solution was added to a DMF solution 0.1 *M* in hydrazine hydrate and light emission was observed.[10] The second procedure involved preparing the radical bromide salt. The salt was added to a DMF solution, 0.1 *M* in hydrazine hydrate, and light was produced. In both cases the blue luminescence was visible in a darkened room to the non-dark-adapted eye. The duration of light emission was about 5–10 sec.

As can be seen from Figure 2, the chemiluminescence spectrum does not exactly match the fluorescence spectrum of 1,6-diaminopyrene. The difference cannot be attributed to self-absorption since the rising portions of the curves are identical. More experimental data are needed before the origin of this long-wavelength component can be completely explained. The chemiluminescence and fluorescence were obtained similarly to those for the ruthenium complexes except that an EMI-9558B photomultiplier tube was used.

We believe that these results, combined with earlier studies,[7] indicate that electron-transfer reactions involving a potentially fluorescent acceptor show great promise for discovering new chemiluminescent systems. A detailed investigation of the mechanism of both reactions reported in this communication is continuing. Experimental details will be published at a later date.

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## Five-Coordinate Complexes. II.[1] Trigonal Bipyramidal Copper(II) in a Metal Atom Cluster

*Sir:*

We wish to report the preparation, properties, and structure of an unusual triphenylphosphine oxide complex of copper(II); the structure, which has been definitely established by a single-crystal X-ray analysis, consists of a metal atom cluster. However, no metal–metal bonding, superexchange, or other interaction between the copper atoms is indicated by the structure nor by the properties of the compound.

When dichlorobis(triphenylphosphine oxide)copper(II) was refluxed in methyl isobutyl ketone, the initial yellow color gradually changed to orange; well-formed orange crystals of $Cu_4OCl_6(TPPO)_4$ (in formulas, TPPO represents triphenylphosphine oxide) were deposited over a period of several days. *Anal.* Calcd for $Cu_4Cl_6P_4O_5C_{72}H_{60}$: Cu, 15.92; Cl, 13.33; P, 7.76; C, 54.17; H, 3.80. Found: Cu, 16.21; Cl, 13.55; P, 7.41; C, 53.61; H, 3.64.

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(9) H. Scott, P. L. Kronick, P. Chairge, and M. M. Labes, *J. Phys. Chem.*, **69**, 1740 (1965).

(10) Sodium naphthalenide can be used as a reducing agent if the solvent employed is tetrahydrofuran.

(1) Part I: J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966).

The crystals are cubic with one molecule per unit cell, $a = 12.22$ A, and of space group symmetry $P\bar{4}3m$. Three-dimensional X-ray data were collected with a precession camera using Mo $K\alpha$ radiation. A Patterson synthesis provided coordinates for all atoms of the asymmetric unit ($CuOClOPC_6H_5$) except the atoms of the phenyl group; an electron density synthesis then revealed the carbon atom positions, some of which were disordered. Subsequent least-squares refinement yielded a final discrepancy factor, *R*, of 10%. Details of the structure determination will be published elsewhere.

The structure of the cluster is shown in Figure 1; triphenylphosphine oxide is represented by L in the figure. The central oxygen is at the center of a tetrahedron of copper atoms with a Cu–O distance of 1.90 A. Between each pair of copper atoms, there is a bridging chlorine atom with a Cu–Cl distance of 2.38 A; the six chlorine atoms form an octahedron around the central oxygen. Attached to each copper and completing a slightly distorted trigonal bipyramid around the copper is the oxygen of a triphenylphosphine oxide with a Cu–O distance of 1.89 A; the Cl–Cu–O(P) angle is 95°, indicating that the copper is displaced slightly from the trigonal plane of chlorine atoms. The space group symmetry requires a linear arrangement of the O, Cu, O(P), and P, and the bond angle at the oxygen of the phosphine oxide is, thus, 180°. The Cu–Cu distance of 3.11 A is too large for direct metal–metal bonding.

Although some interaction through the oxygen was expected, the magnetic moment of 2.21 BM is normal[2] and no interaction is apparent.

The spectrum in the visible and near-infrared region was obtained for a mull and for an acetone solution; there was little difference in the two, suggesting that the cluster also exists in acetone solution. The spectrum shows a broad absorption band at *ca.* 11,000 $cm^{-1}$. This is shifted slightly from the position found for the trigonal bipyramidal $CuCl_5^{3-}$ ion[3,4] (*ca.* 10,000 $cm^{-1}$); the direction of the shift is consistent with the stronger ligand field effect of oxygen as compared to chlorine.

The P–O stretching frequency (1194 $cm^{-1}$) is considerably higher than that found for other complexes of triphenylphosphine oxide.[5] The linear P–O–Cu arrangement found for this compound results in better overlap of the phosphorus and copper $d_{xz}$, $d_{yz}$ orbitals with the $p_x$, $p_y$ orbitals of oxygen and, thus, allows more transfer of electron density to phosphorus than is possible when the P–O–M arrangement is bent, as in $[(CH_3)_3PO]_2Co(NO_3)_2$.[6]

The source of the central oxygen in the preparation of the compound has not been established, but it probably comes from small amounts of water present in the system. The compound can also be prepared from $CuCl_2$, CuO, and triphenylphosphine oxide in either methanol or nitromethane. A stoichiometric amount of CuO was added, but in all preparations some solid CuO remained unreacted.

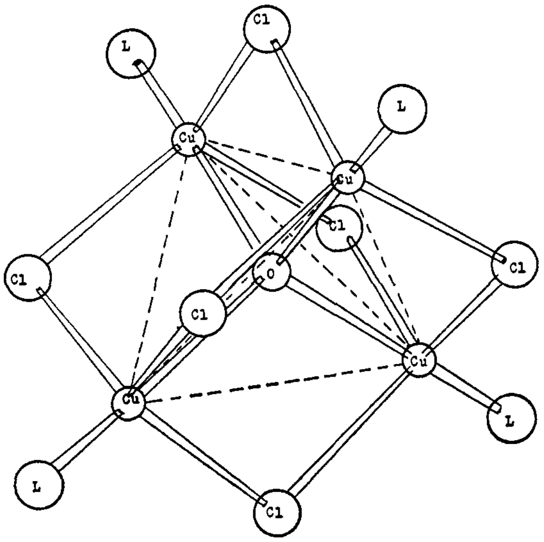

Figure 1. Perspective drawing of the structure of $\mu_4$-oxo-hexa-$\mu$-chloro-tetrakis[(triphenylphosphine oxide)copper(II)]. L represents a triphenylphosphine oxide group.

To investigate the possibility of forming related complexes with the formula $Cu_4OCl_6L_4$ (where L represents a monodentate ligand), $(CH_3)_4NCl$ was added to a methanol solution of $CuCl_2$ which had been refluxed with CuO for 24 hr; deep red crystals of $[(CH_3)_4N]_4Cu_4OCl_{10}$ were obtained. *Anal.* Calcd for $Cu_4Cl_{10}ON_4C_{16}H_{48}$: Cu, 27.58; Cl, 38.48; C, 20.85; H, 5.26. Found: Cu, 27.77; Cl, 38.10; C, 21.00; H, 5.22.

The spectral and magnetic properties of this compound are very similar to those of the triphenylphosphine oxide complex, and a similar cluster, with chlorides replacing the triphenylphosphine oxide groups, is probably present. The crystals are also cubic, but a much larger unit cell was found ($a = 19.04$ A). The structure of this compound is presently being investigated.

Investigations of related copper compounds are in progress; attempts to prepare similar compounds of other transition metals have been unsuccessful but are also continuing.[6a]

**Acknowledgment.** This work was supported by the National Science Foundation under Grant No. GP 3826. The help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is gratefully acknowledged.

[6a] NOTE ADDED IN PROOF. The structure of a magnesium compound, $Mg_4OBr_6(C_4H_{10}O)_4$, with a similar cluster has been reported by G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

[7] Alfred P. Sloan Research Fellow, 1966–1968.

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*Received August 8, 1966*

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[5] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[6] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

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## Concerning Structural Limitations in the Relationship between Trityl Cation Stability and Reactivity[1]

*Sir:*

The very rapid reaction rates of unstable carbonium ions with nucleophiles has limited our knowledge of their reactivities to (1) relative rates or (2) solvolysis

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[1] This research has been supported in part by the National Science Foundation.