concentration of radical dimer **2**; magnesium cation stabilizes the aminyl radical analogous to its stabilization of TM-3.[11] With an excess of oxygen, **5** reached its maximum concentration long after 99% of **2** had been oxidized to **4**.[12] At this point addition of **2** resulted in the rapid disappearance of the three-line EPR signal of **5** and the appearance of the 24-line signal of TM-3. Although peroxide **6** was not visible by ^{1}H NMR, its formation is consistent with the formation of peroxides from reaction of triphenylmethyl with oxygen.[13]

The reversibility of oxidation of **2** is proposed because reaction of oxazinone **4** with hydrogen peroxide gave a persistent radical showing a three-line EPR signal identical with the signal assigned to aminyl **5**. The intensity of the signal was comparable to the intensity observed for the air oxidation of **2** at equivalent concentrations, and the same EPR signal was observed by using hydrogen peroxide labeled with ^{17}O.[14] Mixing of solutions containing equal concentrations of the persistent radical from oxidation of **2** with oxygen and reaction of hydrogen peroxide with **4** gave a solution showing a single three-line EPR signal with the same intensity. Furthermore, freeze, pump, thaw degassing of solutions of aminyl **5** formed from **2** and oxygen after consumption of **2** increased the rate of disappearance of the aminyl EPR signal.[12] The reversible formation of bis(triarylmethyl) peroxides has been established.[15]

The reversibility of the oxidation of **2** was consistent with the relative maximum EPR signal intensities for **5** resulting from different initial concentrations of **2**. The mechanism in Scheme I predicts that $[\mathbf{5}] = K_c[\mathbf{4}][H_2O_2]^{1/2}$ where K_c is a composite equilibrium constant. Solutions of **2**, 0.06, 0.08, and 0.12 M, in ethanol containing 0.32 M magnesium perchlorate were reacted with oxygen to completion; the EPR signal heights were measured; and the resulting concentrations of **4** and hydrogen peroxide were determined. The measured and calculated relative signal intensities were 1:2.5:5.7 and 1:2.1:4.8, respectively. The signal intensity starting with 0.08 M **2** indicated that the maximum concentration of **5** was approximately 1×10^{-5} M by comparison with standard solutions of 4-oxo-2,2,6,6-tetramethylpiperidinoxy.

The formation and persistence of **5** appears to be anomalous. Aminyl radicals are in general less persistent than **5** unless resonance stabilized, show *g* values in the range of 2.004–2.005 with a_N = 12.5–16 G, and react with molecular oxygen.[16] The half-life of 2,2,6,6-tetramethylpiperidinyl at 24 °C is less than 35 s.[10] Gas-phase N–H and O–H bond energies for simple secondary amines and hydrogen peroxide suggest that $\mathbf{7} \Rightarrow \mathbf{5}$ would be slightly endothermic.[17] Possibly, intramolecular hydrogen bonding to the hydroperoxy functional group provides some additional stabilization of **5** and gives rise to the high *g* value. 2-Aminophenoxy, *o*-semiquinones and -semidiones,[18] and *tert*-butyl(2-hydroxy-1-phenylethyl)nitroxide[19] have been shown to exhibit intramolecular hydrogen bonding. Although aminyl radicals generally react with oxygen to give nitroxides, an example which does not is 4-oxo-2,2,6,6-tetramethylpiperidinyl.[20]

In summary, we report evidence that oxidation of TM-3 with molecular oxygen yields stoichiometric quantities of hydrogen peroxide with generation of an unusually persistent aminyl radical. We have also found that other radicals of this type, including 3,5-dimethyl-5-hydroxymethyl-2-oxomorpholin-3-yl,[3] 3,5,5-trimethyl-2-oxopiperizin-3-yl,[21] and the oligomers of the diradical bi(3,5,5-trimethyl-2-oxomorpholin-6-yl)-3,3′-diyl,[22] produce persistent aminyl radicals upon exposure to air. The mechanism in Scheme I for oxidation of TM-3 is related to the mechanisms proposed for the air oxidation of dicyclohexylamine,[23] indoles including tryptophan to kynurenine,[24] tetrahydrofolate,[25] and reduced flavins.[26]

Registry No. 1, 57765-64-7; *meso*-**2**, 53153-52-9; (±)-**3**, 53153-53-0; **4**, 53153-46-1; **5**, 103150-35-2.

---

[11] Olson, J. B.; Koch, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 756.

[12] After the EPR signal for **5** reached its maximum, it slowly faded over a period of several days.

[13] Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; p 408.

[14] ^{17}O labeled hydrogen peroxide was prepared by the method of Sawaki and Foote: Sawaki, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 6292.

[15] Janzen, E. G.; Johnston, F. J.; Ayers, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 1176.

[16] Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783.

[17] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[18] Loth, K.; Graf, F. *Helv. Chim. Acta* **1981**, *64*, 1910.

[19] Kotake, Y.; Kuwata, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3686.

[20] Toda, T.; Mori, E.; Horiuchi, H.; Murayama, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1802.

[21] Kleyer, D. L.; Haltiwanger, R. C.; Koch, T. H. *J. Org. Chem.* **1983**, *48*, 147.

[22] Gaudiano, G.; Sweeney, K.; Haltiwanger, R. C.; Koch, T. H. *J. Am. Chem. Soc.* **1984**, *106*, 7628.

[23] Hawkins, E. G. E. *J. Chem. Soc., Perkin Trans. 1* **1972**, 13.

[24] Karnojitzky, V. *Russ. Chem. Rev.* **1977**, *46*, 121. Iddon, B.; Phillips, G. O.; Robbins, K. E. *J. Chem. Soc. B* **1971**, 1887. Jayson, G. G.; Scholes, G.; Weiss, J. *Biochem. J.* **1954**, *57*, 386.

[25] Blair, J. A.; Pearson, A. J. *J. Chem. Soc., Perkin Trans 2* **1974**, 80.

[26] Massey, V.; Ghisla, S. In *34th Colloquim on Biological Oxidations-Mosbach 1983*; Springer Verlag: Berlin, 1983; p 114.

Molecular and Electronic Structure of Cu(tet-b)SSCH$_2$CO$_2$·3CH$_3$OH, a Novel Copper(II) Alkyl Persulfide Complex

Elizabeth John, Parimal K. Bharadwaj,
Karsten Krogh-Jespersen,* Joseph A. Potenza,* and
Harvey J. Schugar*

Department of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

Received February 11, 1986

A few Cu(II) aromatic[1-5] and aliphatic[6,7] thiolate complexes have been structurally characterized; most are transient species having varied decomposition pathways,[8-11] some of which may be blocked. We have crystallized a *cis*-Cu^{II}N$_2$S$_2$ complex[7] ligated by a linked L-cysteine ester [$^-$SCH$_2$(CO$_2$CH$_3$)NHCH$_2$–]$_2$ (**2**); the parent Cu(cysteine)$_2$ complex[11] and ternary Cu(cysteine) complexes[8-10] are quite unstable. We report here a novel Cu(II) thiolate redox reaction that yields a stable Cu(II)–alkyl persulfide complex and provides new structural and spectroscopic guideposts for mechanistic studies.

In an attempt to prepare the mercaptoacetate analogue of Cu(tet-b)SCH$_2$CH$_2$CO$_2$ (**3**),[6] ether was vapor diffused at 6 °C into a filtered solution of 0.5 mM Cu(tet-b)$^{2+}$,[2] 1.3 mM KOH, and 0.65 mM HSCH$_2$CO$_2$H or its dicyclohexylamine salt[12] in 8 mL of methanol. Complex **1** crystallized as thin green plates in

---

[1] Corrigan, M. F.; Murray, K. S.; West, B. O.; Pilbrow, J. R. *Aust. J. Chem.* **1977**, *30*, 2455.

[2] Hughey, J. L.; Fawcett, T. G.; Rudich, S. M.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1979**, *101*, 2617.

[3] Anderson, O. P.; Perkins, C. M.; Brito, K. K. *Inorg. Chem.* **1983**, *22*, 1267.

[4] Aoi, N.; Takano, Y.; Ogino, H.; Matsubayashi, G.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1985**, 703.

[5] Addison, A. A.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 1225.

[6] John, E.; Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.*, in press.

[7] Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 1351.

[8] Davis, F. J.; Gilbert, B. C.; Norman, R. O. C.; Symons, M. C. R. *J. Chem. Soc., Perkins Trans. 2* **1983**, 1763 and references cited therein.

[9] Baek, H. K.; Cooper, R. L.; Holwerda, R. A. *Inorg. Chem.* **1985**, *24*, 1077.

[10] Anderson, C. H.; Holwerda, R. A. *J. Inorg. Biochem.* **1985**, *23*, 29.

[11] Cavallini, D.; DeMarco, C.; Dupre, S.; Rotilio, G. *Arch. Biochem. Biophys.* **1969**, *130*, 354.

[12] The salt was prepared by mixing equimolar amounts of acid and amine in toluene and recrystallized from methanol/petroleum ether in ca. 90% yield (mp 150–54 °C). Anal. Calcd for C$_{14}$H$_{27}$NSO$_2$: C, 61.49; N, 5.12; S, 11.73. Found: C, 61.09; N, 5.05; S, 11.85.

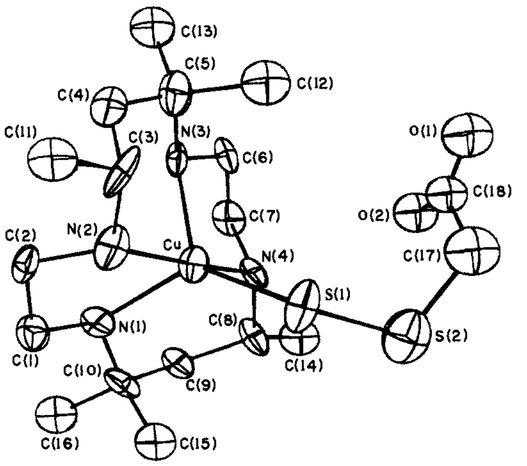

Figure 1. Structure of the title compound (**1**) showing the atom numbering scheme. For clarity, H atoms have been omitted. Selected interatomic distances: Cu-S(1), 2.328 (5); Cu-N(1), 2.128 (13); Cu-N(2), 2.009 (13); Cu-N(3), 2.125 (12); Cu-N(4), 2.000 (11); S(1)-S(2), 2.017 (7); S(2)-C(17), 1.83 (2) Å. Selected angles: S(1)-Cu-N(1), 128.8 (4)°; S(1)-Cu-N(2), 89.0 (4)°; S(1)-Cu-N(3), 125.1 (4)°; S(1)-Cu-N(4), 98.4 (4)°; N(2)-Cu-N(4), 172.5 (6)°; Cu-S(1)-S(2), 113.6 (3)°; S(1)-S(2)-C(17), 99.9 (8)°; Cu-S(1)-S(2)-C(17), torsional, −98.6°.

ca. 14% yield after 12 h.[13] The reaction proceeds most cleanly under strictly anaerobic conditions, although it is not necessary to exclude oxygen rigorously to obtain product. The dry product darkened in minutes when exposed to air; crystals coated with mineral oil or covered with ether were stable for hours while those sealed in capillaries with some methanol appeared to be stable indefinitely. A structural study was performed to account for the different charge-transfer spectra of **1** and **3**.

The structure[14] (Figure 1) contains Cu(II) monomers with trigonal bipyramidal N_4S ligand sets structurally similar to those reported for **3**[6] and Cu(tet-b)(2-mercaptobenzoate) (**4**).[2] The Cu-S distance [2.328 (5) Å] is comparable to those reported for **4** [2.359 (4) Å] and **3** [2.314 (2) Å] and longer than those of **2** [2.230 (5), 2.262 (4) Å]. Equatorial Cu-N distances are longer than the axial distances, a feature probed by a recent theoretical study.[15] Structural features of the hydropersulfide unit fall within the range of those reported for the H_2S_2 parent and for organic disulfides; i.e., S-S and S-C distances of ca. 2.0 and 1.8 Å, respectively, and R-S-S-C dihedral angles of 90 (10)°.[16]

The magnetic moment of **1** at 298 K, corrected for diamagnetism (-329×10^{-6} cgs)[17] and for a protective film of mineral oil, is 1.7 (1) μ_B. Electronic spectra of methanolic **1** (band positions of polycrystalline **1** are similar) include maxima at ~13000 cm^{-1} (ϵ ~700) and ~10500 (sh), which mimic the LF spectra reported for related $Cu^{II}N_4S$ species.[2,6] The near-UV absorptions of **1** at 25 700 cm^{-1} (ϵ ~500) and 21 500 cm^{-1} (ϵ ~760) are too low in energy to be LMCT from the tet-b ligand;[18] aliphatic disulfides, including the parent H_2S_2, do not absorb below 40 000 cm^{-1}.[19] The "simple" thiolate analogues **3** and **4** exhibit prominent absorption at about 27 000 cm^{-1} flanked by weaker absorption at ~23 000 cm^{-1} which have been attributed to σ(thiolate) and π(thiolate) → Cu(II) LMCT, respectively.[2,6] The "reversed" intensity pattern of **1** (relative to **3** and **4**) is reminiscent of LMCT for metal-peroxide complexes.[20]

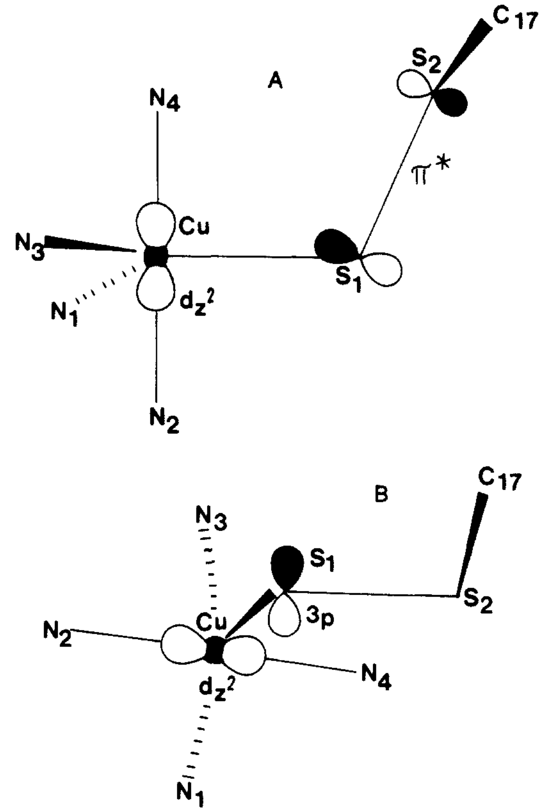

Figure 2. Partial structures of **1** showing (A) the ligand HOMO and Cu(d_{z^2}) vacancy and (B) the ligand SHOMO and Cu(d_{z^2}) vacancy.

Both ab initio and INDO/S calculations reveal that the two highest occupied MO's of a model CH_3SS^- unit are well separated (>15 000 cm^{-1}) from the corelike orbitals and both have their major orbital coefficients on the terminal S center, S(1). The HOMO is a π^* S-S orbital polarized toward the end S and the SHOMO is a 3p-type lone pair lying in the SSC plane, normal to the S-S axis. The reversed EPR spectra ($g_\perp = 2.16$, $g_\parallel = 2.00$, $A_\perp^{Cu} = 90 \times 10^{-4}$ cm^{-1}) of **1** in methanol (80 K) mimic those of CuBr(Me$_6$tren)Br, a Cu(II) complex with a d_{z^2} ground state.[21] Both the ligand HOMO and SHOMO orbitals are oriented approximately perpendicular to the N(2)-Cu-N(4) axis (z), Figure 2. We assign the band at 21 500 cm^{-1} as $S_2(\pi^*) \rightarrow d_{z^2}$ and that at 25 700 cm^{-1} as S(3p) → d_{z^2}. The calculated separation of these ligand orbitals (2000–5000 cm^{-1}) and their poor overlap with the Cu(II) d vacancy (Figure 2) account for the splitting and modest intensity of the LMCT spectra.

The free hydropersulfide molecule should not be stable in methanolic KOH[22] and presumably results from the Cu(II) oxidation of ligated mercaptoacetate. Complex **1** cleanly forms under anaerobic conditions; studies to define the kinetic pathway are in progress.[23]

---

(13) Anal. Calcd for $CuC_{20}H_{46}N_4S_2O_4$, Cu(tet-b)$S_2CH_2CO_2 \cdot 2CH_3OH$: Cu, 11.90; S, 12.00. Found: Cu, 11.98; S, 12.24.

(14) Crystallographic analysis: space group $P2_1/n$, a = 13.920 (6) Å, b = 13.753 (2) Å, c = 14.472 (6) Å, β = 92.25 (3)°, V = 2768 (3) Å^3, Z = 4, d_{obsd} = 1.36 (1) g cm^{-3} in CCl_4/hexane, d_{calcd} = 1.282 g cm^{-3} for $2CH_3OH$ and 1.359 g cm^{-3} for $3CH_3OH$. The structure was solved (1172 reflections, $I > 2\sigma$, $2\theta \leq 41.6°$, Mo Kα radiation) by using the Enraf-Nonius SDP package and refined to discrepancy indexes $R_{F(wF)}$ = 0.092 (0.087) with a final goodness of fit of 1.98. The number of solvate molecules was difficult to determine crystallographically and this is responsible for the relatively high R factors. Only one methanol molecule was crystallographically well-defined. A second was located, but with unusually large (30 (2) and 33 (2) Å^2) temperature factors, while the final difference map showed several peaks of the order of 0.5 e/Å^3 that could be part of another (disordered?) methanol. Elemental analysis, performed on partially dried crystals, suggested a minimum of two methanols while the observed density was consistent with three. We believe that approximately one lattice methanol was lost when the crystals were dried prior to elemental analysis and that the trisolvate is the true formula.

(15) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1984**, *23*, 3853.

(16) Rindorf, G.; Jorgensen, F. S.; Snyder, J. P. *J. Org. Chem.* **1980**, *45*, 5343.

(17) Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976; pp 491–496.

(18) Aqueous Cu(tet-b)·$2ClO_4$ has a UV absorption at 37 000 cm^{-1} (ϵ >5000); see: Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.

(19) Rauk, A. *J. Am. Chem. Soc.* **1984**, *106*, 6517 and references cited therein.

(20) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

(21) Barbucci, R.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2117.

(22) Kawamura, S.; Otsuji, Y.; Nakabayshi, T.; Kitao, T.; Tsurgi, J. *J. Org. Chem.* **1965**, *30*, 2711.

Acknowledgment. The research of H.J.S. and J.A.P. was supported by the National Science Foundation (Grant CHE-8417548), the Charles and Johanna Busch Fund–Rutgers University, and a crystallographic instrumentation grant from the National Institutes of Health (Grant 1510 RRO 1486 01A1). The research of K.K.-J. was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (Grant GM 34111).

Supplementary Material Available: Tables of crystal and refinement data and lists of atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

---

(23) Professor Robert Holwerda, Texas Tech University.

Laser Spectroscopy of Calcium and Strontium Monocyclopentadienide

L. C. O'Brien and P. F. Bernath*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received April 22, 1986

The gas-phase reaction of Ca or Sr vapors with cyclopentadiene has resulted in the laser spectroscopic observation of the metal monocyclopentadienide free radicals, CaCp and SrCp (Cp = C_5H_5). The spectra are interpreted as arising from "open-faced sandwich" complexes of C_{5v} symmetry. Our experimental methods have general utility for the synthesis and characterization of inorganic free radicals.

The cyclopentadienyl ligand is one of the popular and fascinating ligands in inorganic chemistry.[1] The most celebrated molecule containing Cp is ferrocene, Fe(Cp)$_2$, which has a "sandwich" structure.[1] The alkali metals and the heavier alkaline-earth metals form ionic complexes with C_5H_5.[2-5] InCp[6] and TlCp[7] have C_{5v} symmetry in the gas phase. InCp and TlCp are the covalent closed-shell analogues of the ionic free radicals, Ca$^+$Cp$^-$ and Sr$^+$Cp$^-$, that we have discovered.

We have recently observed a large number of Ca-, Sr-, and Ba-containing free radicals with only one ligand, ML (L = OH,[8-11] OCH_3, OCH_2CH_3, $OCH(CH_3)_2$, $O(CH_2)_2CH_3$, $OC(CH_3)_3$,[12] OCN,[13] CHO_2, CH_3CO_2[14,15]). The bonding and electronic structure in these molecules is well described by an M$^+$ ion perturbed by the L$^-$ ligand. The M$^+$ ions are isoelectronic with the alkali atoms so the molecular states can be described in terms of one-electron metal-centered atomic orbitals.

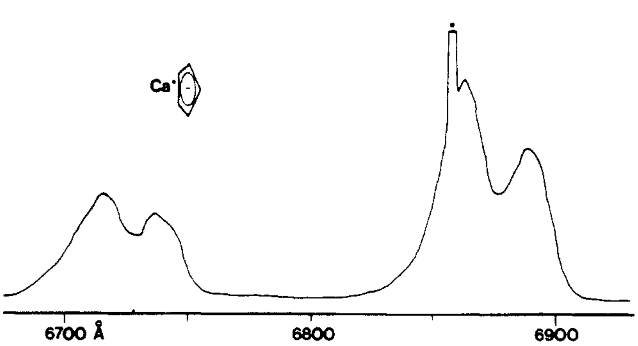

Figure 1. Resolved fluorescence spectrum showing laser-induced fluorescence from the $\tilde{A}$–$\tilde{X}$ transition of CaCp. The splitting between the strong features is due to spin–orbit coupling in the $\tilde{A}^2E_1$ state. The asterisk marks scattered light from the dye laser exciting the molecular transition.

Table I. $\tilde{A}$–$\tilde{X}$ and $\tilde{B}$–$\tilde{X}$ Vibronic Transition Frequencies for CaCp and SrCp in cm^{-1}

	CaCp			SrCp		
band	$\tilde{A}^2E_{1(1/2)}$	$\tilde{A}^2E_{1(3/2)}$	$\tilde{B}^2A_1$	$\tilde{A}^2E_{1(1/2)}$	$\tilde{A}^2E_{1(3/2)}$	$\tilde{B}^2A_1$
3–0	15 495	15 548		14 014^a	14 300	
2–0	15 170	15 226		13 763^a	14 039	
1–0	14 848	14 897	17 072	13 510^a	13 782	15 106
0–0	14 518	14 575	16 772	13 268	13 523	14 846
0–1	14 237	14 282	16 470	13 040	13 289^a	14 616
0–2	13 955	14 002		12 822	13 053^a	
0–3	13 690	13 739				
0–4	13 458^a	13 505^a				

^{a} Blended.

For the Cp$^-$ ligand the ground 4s (Ca$^+$) or 5s (Sr$^+$) atomic orbital gives rise to the $\tilde{X}^2A_1$ ground state of MCp. The excited 3d (Ca$^+$) and 4d (Sr$^+$) atomic orbitals result in d_{z^2} ($^2A_1$); d_{xz}, d_{yz} ($^2E_1$); and d_{xy}, $d_{x^2-y^2}$ ($^2E_2$) states. The expected electronic transitions are B^2A_1–$\tilde{X}^2A_1$ and $\tilde{A}^2E_1$–$\tilde{X}^2A_1$. ($^2E_2$–$^2A_1$ is electric-dipole forbidden.) In fact, the $\tilde{B}^2A_1$ and $\tilde{A}^2E_1$ states are $3d_{z^2}$–$4p_z$ (Ca$^+$) and $4d_{z^2}$–$5p_z$ (Sr$^+$) mixtures because of d–p mixing induced by the C_{5v} ligand field.

MCp (M = Ca, Sr) molecules were produced in a Broida oven[16] by the reaction of the alkaline earth vapor with cyclopentadiene (C_5H_6). Pressures were approximately 1.5 torr of argon and 3 mtorr of cyclopentadiene. The cyclopentadiene was prepared from the Diels–Alder dimer by a simple distillation. The direct reaction of the dimer with Ca vapor was not successful.

A broad-band (1 cm^{-1}) CW dye laser beam was focused into the Broida oven in order to excite the molecular emission. A second broad-band (1 cm^{-1}) dye laser beam was always used to excite the alkaline earth $^3P_1$–$^1S_0$ atomic transition (6892 Å for Sr, 6573 Å for Ca). The reaction was greatly enhanced by electronic excitation of the metal. Two types of experiments were used to record the spectra.

Laser excitation spectra were obtained by scanning the dye laser probing the molecular transitions, and recording the fluorescence through red-pass filters selected to block the scattered laser light. The second dye laser, resonant with the metal atomic line, was chopped to modulate the molecular fluorescence for lock-in detection.

Spectra were also recorded by exciting the molecular emission and recording the resolved fluorescence with a monochromator. For these experiments the molecular emission was imaged onto the entrance slit of a 0.64-m monochromator. Scanning the monochromator (not the laser) provided resolved laser-induced fluorescence spectra.

Figure 1 is a portion of the $\tilde{A}^2E_1$–$\tilde{X}^2A_1$ spectrum of CaCp. This spectrum was recorded by resolving the fluorescence produced by a laser (marked with an asterisk) exciting the $\tilde{A}^2E_{1(3/2)}$–$\tilde{X}^2A_1$

---

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 1163–1167.

(2) Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7–17.

(3) Gowenlock, B. G.; Lindsell, W. E.; Singh, B. *J. Chem. Soc., Dalton Trans.* **1978**, 657–664.

(4) Faegri, K.; Almlof, J.; Luthi, H. P. *J. Organomet. Chem.* **1983**, *249*, 303–313.

(5) Alexandros, S.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 7959.

(6) Shibata, S.; Bartell, L. S.; Gavin, R. M., Jr. *J. Chem. Phys.* **1964**, *41*, 717–722.

(7) Tyler, J. K.; Cox, A. P.; Sheridan, J. *Nature (London)* **1959**, *183*, 1182–1183.

(8) Bernath, P. F.; Kinsey-Nielsen, S. *Chem.* Phys. *Lett.* **1984**, *105*, 663–666.

(9) Bernath, P. F.; Brazier, C. R. *Astrophys. J.* **1985**, *288*, 373–376.

(10) Brazier, C. R.; Bernath, P. F. *J. Mol. Spectrosc.* **1985**, *114*, 163–173.

(11) Kinsey-Nielsen, S.; Brazier, C. R.; Bernath, P. F. *J. Chem. Phys.* **1986**, *84*, 698–708.

(12) Brazier, C. R.; Bernath, P. F.; Kinsey-Nielsen, S.; Ellingboe, L. C. *J. Chem. Phys.* **1985**, *82*, 1043–1045.

(13) Brazier, C. R.; Ellingboe, L. C.; Kinsey-Nielsen, S.; Bernath, P. F. *J. Am. Chem. Soc.* **1986**, *108*, 2126–2132.

(14) Ellingboe, L. C.; Bopegedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *Chem. Phys. Lett.* **1986**, *126*, 285–289.

(15) Brazier, C. R.; Ellingboe, L. C.; Kinsey-Nielsen, S.; Bernath, P. F., manuscript in preparation.

(16) West, J. B.; Bradford, R. S.; Eversole, J. D.; Jones, C. R. *Rev. Sci. Instrum.* **1975**, *46*, 164–168.

0002-7863/86/1508-5017$01.50/0