

distributions for phenyl benzoate reported in Table II include  $d_0$  phenyl benzoate from the cage reaction. Assuming that the cage reaction contributes an absolute yield of 11% to the observed phenyl benzoate yields, Table II, the calculated  $d_0/d_5$  ratios for phenyl benzoate produced from free benzoyloxy radicals are 3.00 and 2.28 for  $1.5 \times 10^{-3}$  and  $7.2 \times 10^{-3}$  M oxygen, respectively.<sup>20</sup> The magnitude of these ratios can only be consistent with considerable C-H bond breaking in the rate-determining step for phenyl benzoate formation. The mechanism in Scheme I yields eq 4,

$$\frac{k_2^H K_1^H}{k_2^D K_1^D} = \frac{[C_6D_6] \left( 1 + \frac{k_2^H}{k_{-1}^H} [O_2] \right)}{[C_6H_6] \left( 1 + \frac{k_2^D}{k_{-1}^D} [O_2] \right)} \left( \frac{d_5}{d_0} - \frac{[C_6HD_5]}{6[C_6H_6]} \right)^{-1} \quad (4)$$

which relates the  $d_5/d_0$  ratio of the phenyl benzoate formed outside the cage with the oxygen concentration, the solvent composition, and the rate constants.

Equation 4 can be used to solve for  $(k_2^H K_1^H/k_2^D K_1^D)$  by assuming different values of  $k_1^H/k_1^D$ . A value of  $(k_2^H K_1^H/k_2^D K_1^D) = 3.1$  at  $30^\circ$  is obtained, which is insensitive to small deviation of  $k_1^H/k_1^D$  from unity. Since  $K_1^H/K_1^D$  is not expected to be significantly different from unity, the ratio reflects mainly the normal isotope effect in the rate constant for the abstraction step,  $k_2$ .<sup>21</sup>

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(20) For example, in the case of  $7.2 \times 10^{-3}$  M oxygen 11% of the phenyl benzoate is produced by the cage process and the remaining 35% by the noncage process. If  $x$  is the fraction of phenyl benzoate- $d_0$  produced outside the cage, then  $(d_0/d_5)_{\text{obsd}} = (0.11 + 0.35x)/0.35(1-x)$ , and using the observed  $d_0/d_5$  ratio in Table II,  $x = 0.695$ . It follows that in this case the  $d_0/d_5$  ratio of the phenyl benzoate produced outside the cage is 2.28.

(21) The much smaller deuterium isotope effect observed for an intramolecular attack of the *o*-phenylbenzoyloxy radical to give the corresponding lactone suggests that cyclization is rate determining in that case.<sup>22</sup>

(22) D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, **80**, 3289 (1958).

(23) National Institutes of Health predoctoral fellow, 1966-1969.

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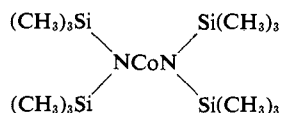
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## Bis(hexamethyldisilylamino)cobalt(II), a Two-Coordinated Cobalt Compound

Sir:

Recently tris(hexamethyldisilylamino)iron(III) was shown to be a monomer giving rise to the unusual coordination number of three for the iron atom.<sup>1</sup>

As part of a continuing study of low-coordination metal-nitrogen compounds we have investigated bis(hexamethyldisilylamino)cobalt(II) which had previously



(1) D. C. Bradley, M. B. Hursthouse, and P. F. Rosesiler, *Chem. Commun.*, 14 (1969).

been prepared by Wannagat and Bürger,<sup>2</sup> but not completely characterized.

The high volatility (bp  $101^\circ$  (0.6 mm)), the high solubility in nonpolar solvents, and the reactivity to water and oxygen suggested that this compound was possibly monomeric with cobalt exhibiting the unusual coordination number of two.

We have determined its molecular weight both in cyclohexane (cryoscopically) and mass spectroscopically. It is monomeric in solution and gave a parent ion at  $m/e$  379 which is consistent with a monomer in the gas phase.

The uv and visible spectra were obtained in dilute hexane solution, in the crystalline state, and in the liquid phase. Attempts are being made to obtain a gas-phase spectrum. All the spectra were very similar indicating that the coordination number probably remains the same in each state. The results are shown in Table I and are compared with those obtained for

**Table I.** Ultraviolet and Visible Spectra (Absorption Maxima  $\text{cm}^{-1}$ )

Dilute soln	Solid	Liquid	CoCl <sub>2</sub> (gas)	Assignment for CoCl <sub>2</sub>
		31,300		
24,400	20,600	24,400	19,000	${}^4\Sigma_g^- \rightarrow {}^4\pi_g(P)$
17,100	17,200	17,000	14,500	${}^4\Sigma_g^- \rightarrow {}^4\Sigma_g^-(P)$
14,600	14,700	14,700	10,300	${}^4\Sigma_g^- \rightarrow {}^4\Delta_g(F)$
6,500			4,000	${}^4\Sigma_g^- \rightarrow {}^4\pi_g(F)$

gaseous cobalt chloride. The uv and visible spectra of gaseous cobalt chloride have been interpreted assuming  $D_{\infty h}$  symmetry in a ligand field formalism.<sup>3,4</sup>

Comparing the ligand field strengths in vanadium(IV) compounds has shown that the ligand field strength of the NR<sub>2</sub> group is much larger than that of Cl.<sup>5</sup> Assuming this also to be the case for cobalt, then the assignments shown in Table I seem reasonable on the basis of a linear NCoN system.

The corresponding compounds of zinc, cadmium, and mercury have been shown (by a normal coordinate analysis of the liquid ir and Raman spectra) to have linear NMN systems.<sup>6</sup> The ir spectrum of the carbon tetrachloride solution of the cobalt silylamide is shown in Table II and compared with the spectrum of the

**Table II.** Ir Spectra<sup>a</sup>

Co, $\text{cm}^{-1}$	Zn	Assignments
1258 vs	1268 s (sh)	$\delta_s(\text{CH}_3)$
1247 vs	1257 vs	$\delta_s(\text{CH}_3)$
995-985 vs	985 vs	$\nu_{\text{as}}(\text{NSi}_2)$
840-830 vs	835 vs	$\rho(\text{CH}_3)$
672 s	674 s	$\nu(\text{SiC}_3)$
615 m	612 m	$\nu(\text{SiC}_3)$
362 s	436 s	$\nu_{\text{as}}(\text{MN}_2)$

<sup>a</sup> vs = very strong, s = strong, m = medium,  $\nu_s$  = symmetric bending,  $\nu_{\text{as}}$  = asymmetric stretching,  $\rho$  = rocking mode, sh = shoulder,  $\delta_s$  = symmetric deformation.

(2) H. Bürger and U. Wannagat, *Monatsh. Chem.*, **94**, 1007 (1963).

(3) J. T. Hougen, G. E. Leroi, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).

(4) C. W. DeKock and D. M. Gruen, *ibid.*, **44**, 4387 (1966).

(5) E. C. Alyea and D. C. Bradley, *J. Chem. Soc. A*, 2330 (1969).

(6) H. Bürger, W. Sawodny, and U. Wannagat, *J. Organometal. Chem.*, **3**, 113 (1965).

zinc compound as assigned by Bürger, Sawodny, and Wannagat.<sup>6</sup> The spectra are very similar except for the metal–nitrogen asymmetric stretching vibrations (Co, 362  $\text{cm}^{-1}$ ; Zn, 436  $\text{cm}^{-1}$ ). The much lower force constant suggesting weaker M–N bonds is consistent with the apparent lower thermal stability of the cobalt compound compared with the zinc compound.

The magnetic susceptibility was determined by the Gouy method over the temperature range 300–80°K and the Curie plot gave a magnetic moment of 4.83 BM independent of temperature. The orbitally non-degenerate ground state ( $^4\Sigma_g^-$ ) would be consistent with this result ( $\mu_{\text{eff}}$  independent of temperature). The large deviation from the spin only value indicates that either there is a very large TIP contribution or large spin–orbit coupling. The latter would seem most probable as the ligand field splitting by two nitrogens would not be expected to be large, thus allowing the “mixing-in” of nondegenerate excited states.

The cobalt silylamide is the only thermally stable dialkylamide of cobalt(II) so far prepared. Attempts to prepare  $\text{Co}[\text{N}(\text{C}_2\text{H}_5)_2]_2$  gave a low yield of bis(*N,N*-diethylbutane-2,4-diiminato)cobalt(II).<sup>7</sup> Larger alkyl groups such as isopropyl gave green hexane-soluble compounds which were thermally unstable and difficult to purify, but which reacted with alcohols to yield alkoxides.

The cobalt silylamide reacted with alcohols forming alkoxides which are under investigation as they appear to exhibit unusual properties. Carbon disulfide reacts with metal dialkylamides to form *N,N*-dialkyldithiocarbamates but it does not appear to give a straightforward reaction with the cobalt silylamide. With oxygen the cobalt complex forms a black polymeric liquid, but with nitric oxide it reacts to form a nitrosyl complex similar to the chromium dialkylamides.<sup>8</sup>

We conclude from the above evidence that  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$  is a monomeric two-coordinate compound of cobalt, but a single-crystal X-ray structure is planned to determine the structural details. The coordinatively unsaturated nature of this cobalt complex suggests reactivity with a variety of small donor molecules and also makes this compound useful for preparing other cobalt compounds not easily prepared by other methods (*e.g.*, the alkoxides).

**Acknowledgment.** One of us (K. J. F.) thanks Queen Mary College for a research studentship.

(7) R. Bonnett, D. C. Bradley, and K. J. Fisher, *Chem. Commun.*, 886 (1968).

(8) D. C. Bradley and C. W. Newing, *ibid.*, 219 (1970).

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## Tunable Ultraviolet Laser Excitation of Formaldehyde. An Application of Nonlinear Optics in Chemistry

Sir:

Monochromatic excitation of molecules has long been a powerful tool in the study of chemistry. How-

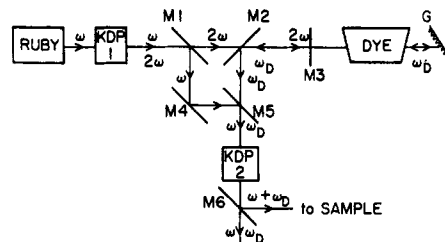


Figure 1. Apparatus for producing tunable uv radiation: (M1) 99% R at 6943 Å, 90% T at 3471 Å; (M2) 90% R at 5200–6500 Å, 85% T at 3471 Å; (M3) 16% R at 5200–6500 Å, 85% T at 3471 Å; (M4) 99.9% R at 6943 Å; (M5) 99% R at 6943 Å, 90% T at  $\leq 6000$  Å; (M6) 95% R at 3000–3500 Å, 95% T at 5000–7000 Å.

ever, past methods have been based either on selected atomic lines, thus sacrificing tunability, or on separating out portions of a spectrally broad light source, thus sacrificing spectral bandwidth. The first lasers offer high peak powers as well as great spectral radiance, but are still limited to fixed wavelengths. With the recent advances in tunable lasers and in nonlinear optics, we have been able to develop a continuously tunable uv source with power output in the 100–200-kW range for pulses of 7-nsec (FWHM) duration and a spectral bandwidth of 1 Å (FWHM). With this light source, we have excited gaseous dideuterioformaldehyde ( $\text{D}_2\text{CO}$ ) and have been able to obtain, through fluorescence decay, the lifetimes of known vibrational levels of the first singlet excited state.

Our tunable uv source is based on obtaining a summation frequency by mixing in a nonlinear crystal<sup>1</sup> the 6943-Å output of a ruby laser and the continuously tunable output of an organic dye laser.<sup>2</sup> The optical arrangement used is shown in Figure 1.

A Pockels cell Q-switched giant-pulse ruby laser<sup>3</sup> produces 90 MW of 6943-Å radiation 25 nsec in duration. The ruby fundamental ( $\omega$ ) passes through a 1-in. long KDP (potassium dihydrogen phosphate) crystal cut  $50^\circ 35'$  from the *c* axis (KDP1) and generates phase-matched<sup>1</sup> second harmonic radiation ( $2\omega$ ) at 3471 Å with 6-MW power and 15-nsec duration as measured with a TRG 108 thermopile. The second harmonic light is separated from the ruby fundamental by M1 and proceeds *via* M2 and M3 into the dye cell to pump the dye laser. The dye-laser cavity consists of an output mirror M3 with a 16% broad-band reflectance, a Bausch and Lomb grating blazed at 5000 Å (Littrow operation) with 1800 grooves/mm, and a 1-in. diameter, 0.75-in. long cylindrical dye cell with AR-coated  $1/16$ -in. thick quartz windows. We find that to ensure high output powers and narrow spectral spreads from the dye laser, the outer cylindrical wall of the cell must be frosted by grinding with carborundum, and the end windows must be tilted  $5^\circ$  off parallel, so that neither is parallel to M3. The summing process is polarization sensitive; the grating is placed with the grooves perpendicular to the direction of polarization of the ruby fundamental.<sup>4</sup> For some dyes, it is neces-

(1) (a) D. A. Kleinman, *Phys. Rev.*, **128**, 1761 (1962). (b) G. C. Baldwin, "An Introduction to Nonlinear Optics," Plenum Press, New York, N. Y., 1969, p 155.

(2) (a) B. H. Soffer and B. B. McFarland, *Appl. Phys. Lett.*, **10**, 266 (1967); (b) B. B. Snavely, *Proc. IEEE*, **57**, 1374 (1969); (c) F. P. Shafer, *Ber. Bunsenges. Phys. Chem.*, **73**, 773 (1969).

(3) (a) F. P. Burns, *IEEE Spectrum*, **4**, 115 (1967); (b) W. Kleen and R. Muller, "Laser," Springer-Verlag, Berlin, 1969.