

Fig. 3.—Absorption (solid line), fluorescence (dashed line), and polarization ratio of adenine.

face changes toward the high frequency side of the first band, which may indicate intermediate coupling. An additional possibility is that high vibronic transitions in the first band can be perpendicularly polarized owing to the nearness of a second band. We have measured the polarized fluorescence here as a sort of blank and find that the polarization ratio stays up at around +0.4 considerably farther across the band than in the case of adenine. Apparently selective borrowing for dimethoxybenzene is absent; perhaps also then for adenine. The ratio could be changed by the overlapping tail of the next strong band, but quantitative consideration from this point of view requires postulating a tail having an implausible shape. Thus there appears to be a weak second transition. According to our quantitative consideration of the depolarization, the second transition would have a maximum extinction coefficient about one-tenth that of the first transition. All this harmonizes with, and, we believe, tangibly reinforces the conclusions of Mason, Stewart and Davidson, and Clark and Tinoco.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

PATRICK R. CALLIS
EUGENE J. ROSA
WILLIAM T. SIMPSON

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The Tetrameric Structure of Anhydrous, Crystalline Cobalt(II) Acetylacetonate

Sir:

Structural investigations of β -ketoenolate complexes of various transition metals have sometimes revealed interesting and unsuspected complications.^{1,2} We report here the rather novel and complicated structure of anhydrous, crystalline bis(2,4-pentanedione)cobalt(II). It was recently reported that this compound in solution in noncoordinating solvents exists in polymeric equilibrium, with oligomers at least as large as $[\text{Co}(\text{AA})_2]_4$. The monomer was considered to be tetrahedral but the oligomers were believed to have the metal atoms in distorted octahedral environments.³

(1) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

(2) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc. (London)*, **A254**, 205 (1960); **A254**, 218 (1960).

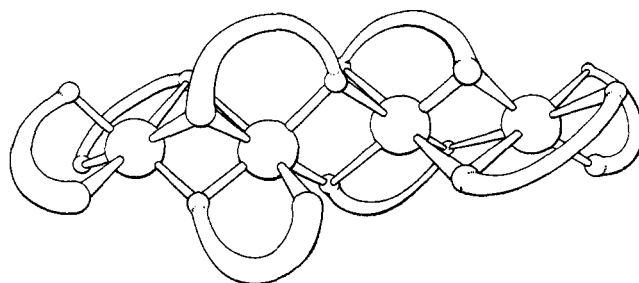


Fig. 1.—A schematic diagram of the structure of $[\text{Co}(\text{AA})_2]_4$. The O-C-C-O rings are indicated by curved lines.

The anhydrous crystals are prepared only with difficulty by sublimation⁴ (~ 2 mm. at $\sim 100^\circ$) and we have yet to discover a crystal which is not twinned and/or cracked.⁵ From one crystal which was twinned but not seriously cracked, all data were obtained.

The triclinic unit cell has the dimensions: $a = 8.61$, $b = 10.38$, $c = 13.72$ Å.; $\alpha = 93^\circ 50'$, $\beta = 90^\circ 25'$, $\gamma = 98^\circ 35'$; there are four $\text{Co}(\text{AA})_2$ groups in the unit cell. The intensities of 880 reflections were visually estimated from precession photographs on which the interpenetrating reciprocal lattices could be separately indexed. The accuracy of these data is not as good as would normally be expected because of the poor quality of the crystal. A Patterson function showed the positions of the cobalt atoms and indicated that the space group is the centric one. A first Fourier map phased on the cobalt atoms revealed the oxygen atoms, and a second Fourier map phased on both cobalt and oxygen atoms provided trial positions for all of the carbon atoms. In the course of five cycles of least-squares refinement, the residual dropped steadily from 37 to 25%.

The structure is that of a tetramer (Fig. 1), which is centrosymmetric. There are three distinct types of rings: those with both oxygen atoms bonded to only one terminal cobalt atom, those with one oxygen atom serving as a bridge between two cobalt atoms, and those with both oxygen atoms serving as bridges. In a general way, though *not* in detail, the structure can be thought of as consisting of two fragments of the $[\text{Ni}(\text{AA})_2]_3$ structure¹ with a common octahedral edge. This structure is consistent with the previously reported³ study of solutions. The apparent leveling off of the polymerization number at a value of 2 at high concentrations at CCl_4 at 77° may represent a genuine stability of the dimeric unit $[\text{Co}(\text{AA})_2]_2$, or it may show that the presence of traces of coordinating impurities (*e.g.*, alcohols, ether, H_2O) tends to split the tetramers into dimers in which each metal atom achieves a coordination number of six.

On the basis of the structure reported here for $[\text{Co}(\text{AA})_2]_4$ and that previously found for $[\text{Ni}(\text{AA})_2]_3$, the structures of the $[\text{M}(\text{AA})_2]_2\text{py}$ ($\text{M} = \text{Co}, \text{Ni}$) compounds prepared by Fackler⁶ might very well correspond, in general if not in detail, to one-half of the $[\text{Co}(\text{AA})_2]_4$ molecule, with one of the nonbridging coordination sites filled by the pyridine molecule.

(3) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

(4) It is extremely difficult, if not impossible without extraordinary precautions, to dry solvents sufficiently to obtain completely anhydrous material by crystallization from solution.

(5) Over fifty were examined on the precession camera; they are exceedingly fragile, cracking under the slightest stress.

(6) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962); *Inorg. Chem.*, **2**, 266 (1963).

An investigation of this is under way. A detailed report of the present study will be submitted when refinement is complete.

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DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

F. A. COTTON
R. C. ELDER

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p-Carborane [1,12-Dicarboclovododecaborane(12)]

Sir:

Two of the three possible geometrical isomers for the icosahedral carborane system,¹ carborane (*ortho*) and neocarborane (*meta*), have been reported²⁻⁵ and variously studied. Assignment of structure has been made principally by comparison of the observed ¹¹B n.m.r. spectra of these two isomers and their decachloro derivatives to those theoretically deduced for them.⁶ We now wish to report the synthesis and identification of the third possible isomer, *p*-carborane.

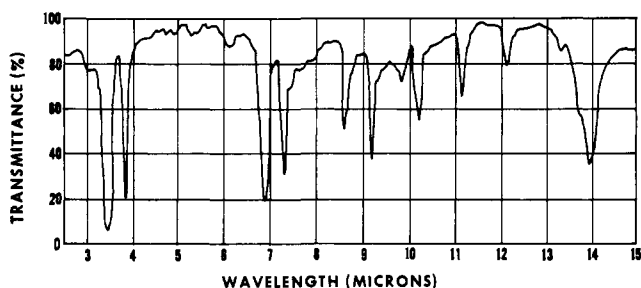


Fig. 1.—Infrared spectrum of *p*-carborane (Nujol mull).

While studying the thermal behavior of neocarborane which undergoes gross decomposition at 630°, it was observed that unfamiliar infrared absorptions appeared in samples which had been held at 500–620° for several hours.⁷ To investigate further, 2.3 g. of neocarborane was placed in a nitrogen-flushed, 100-ml. stainless steel autoclave and heated at 615° for 17 hr. Sublimation of the residue (50° at 0.1 mm.) yielded 0.29 g. of sublimate. This sublimate was dissolved in 0.4 ml. of benzene and subjected to vapor phase chromatography at 150° using a 5 ft. column packed with 20% silicone SF-96 on firebrick. Two components were separated; the component first released was *p*-carborane followed rather closely by neocarborane. Carborane was found to pass through the column much more slowly and none was detected in the mixture above. *Anal.* Found for C₂B₁₀H₁₂: C, 17.1; H, 8.4.; B, 75.4. The *p*-carborane was recovered in 6.5% yield and melted at 259–261°.⁸

- (1) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).
- (2) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).
- (3) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).
- (4) L. I. Zakharkin, V. I. Stanko, V. A. Bratdsv, Y. A. Chapovskii, and Y. T. Dstruchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11**, 2069 (1963).
- (5) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).
- (6) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).
- (7) For infrared spectra of carborane and neocarborane, see H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963); and ref. 5.
- (8) Various melting points have been observed and reported for carborane and neocarborane. It has been our experience that their observed melting points are markedly influenced by the technique used, probably because of their extreme tendency to sublime. For purposes of comparison here we

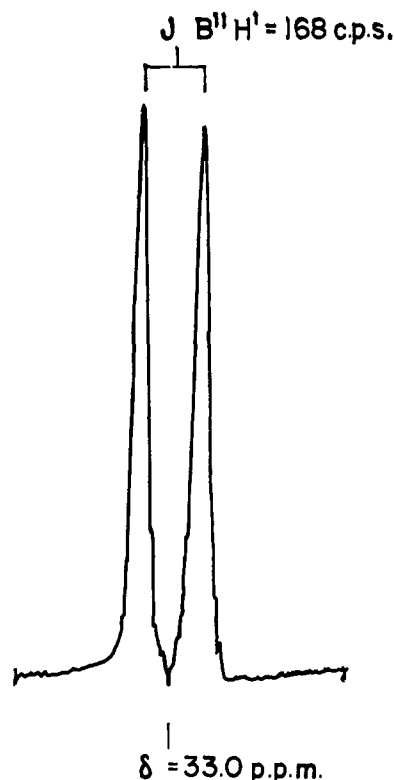


Fig. 2.—¹¹B n.m.r. spectrum of *p*-carborane in deuteriochloroform; displacement from methyl borate (external).

The mass spectrum of *p*-carborane was typical of a carborane derivative with the expected cut-off peak appearing at 144 mass units. Although we have not attempted detailed assignments, the infrared spectrum (Fig. 1) is characteristically different from those of carborane and neocarborane in the 8.2–12.2 μ range. Conclusive proof of the *para* or 1-12 carbon orientation was obtained from the ¹¹B n.m.r. spectrum (Fig. 2) which consisted of only one doublet arising from the ten geometrically equivalent boron atoms. On decoupling this doublet collapsed to a singlet. This is in accord with the theoretical spectrum deduced by Schroeder and Vickers⁶ for a *p*-carborane.

Additional investigations in this area are in progress and will be reported in detail subsequently.

Acknowledgments.—The authors wish to thank Mr. G. D. Vickers for obtaining and examining the various n.m.r. spectra needed. This work was sponsored by the Office of Naval Research.

sealed off small sections of capillary tubes which were well filled with material and determined the melting points simultaneously using a Mel-Temp apparatus. Under these conditions we found for carborane 294–296°, neocarborane 272–273°, and *p*-carborane 259–261°. NOTE ADDED IN PROOF.—Dr. W. N. Lipscomb suggests that these variations in melting points could be associated with different amounts of partial ordering of the cubic structures of the carboranes in the solid state.

ORGANICS DIVISION
OLIN MATHESON CHEMICAL CORPORATION
NEW HAVEN, CONNECTICUT

STELVIO PAFETTI

THEODORE L. HEYING

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Computer Search for Active Site Configurations¹

Sir:

The covalent bond structure of many large biological polymers such as the proteins insulin, ribonuclease,

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