taining a polynitratometal ion, although it is not unlikely that others exist. It is to be noted that in his work on the preparation of anhydrous metal nitrates Addison[3] obtained a compound $Zn(NO_3)_2 \cdot N_2O_4$ for which he suggested the structure $(NO^+)_2[Zn(ONO_2)_4]$ and he also mentions isolating $Co(NO_3)_2 \cdot 2N_2O_4$ (red-purple) which is presumably of the same nature. It would appear worthwhile to attempt the preparation of other compounds containing $[M(ONO_2)_x]$ anions either by the simple method suggested here or by other metathetical reactions. However, we do not plan to undertake such studies in This Laboratory.

Our particular object in preparing this compound was to examine its spectral properties and electronic structure parameters. It recently has been shown[4] that there are tetrahedral complexes of Co(II) which have rather small decrements in the interelectronic repulsion parameter, B, and rather low electronic absorption band intensities. Since several of these are of the type $CoL_2(ONO_2)_2$ it seemed likely that the tetrahedral $[Co(ONO_2)_4]^{2-}$ ion should also have these properties. From the electronic spectrum we obtain[2] $\Delta = 4660$ cm.$^{-1}$, $B = 855$ cm.$^{-1}$ and $f(\nu_3) = 1.94 \times 10^{-3}$. Thus on the previously reported plot of ΔB *vs.* $f(\nu_3)$,[5] the point for $[Co(ONO_2)_4]^{2-}$ falls very close to the best line through the points for the other compounds. It is also interesting that the Δ value places the nitrate ion further toward the strong end of the spectrochemical series than are other oxygen-coördinating ligands.

We are grateful to the U. S. Atomic Energy Commission and the Alfred P. Sloan Foundation for financial aid.

(3) C. C. Addison and B. J. Hathaway, "Recent Aspects of the Inorganic Chemistry of Nitrogen," the Chemistry Society, London, Special Publication No. 10, 1957, p. 41.

(4) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).

(5) $\Delta B = 967 - B$.

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RECEIVED MARCH 31, 1962

TETRAHEDRAL COMPLEXES CONTAINING NITROGEN-TO-NICKEL BONDS[1]

Sir:

We are unaware of any evidence previously reported for a tetrahedral configuration for solid complexes containing nitrogen-to-nickel bonds. The infrared spectrum of dark green diiodobis-(pyridine)-nickel(II) was observed to be characteristic of tetrahedral compounds of the type Mpy_2X_2, particularly in the position of the absorption associated with the C–H in-plane bending vibration at 1068 cm.$^{-1}$ and the splitting (755 and 753 cm.$^{-1}$) associated with coupling between C–H out-of-plane bending vibrations in adjacent pyridine rings. A typical splitting also was observed in the 700 cm.$^{-1}$ region, with peaks at 693 and 689 cm.$^{-1}$. The spectrum differed in these respects from those of the bridged, octahedral dichloro and dibromo complexes. The visible and near infrared spectra in a potassium bromide disk and benzene solution revealed absorption in the 600 and 900 mμ regions characteristic of tetrahedral nickel(II) complexes. The absorption maxima in millimicrons observed in benzene solution (molar extinction coefficients in parentheses) are: 405(2060), 455(2220), 575-(320), 925(90), and 1000(110). A magnetic moment of 3.44 Bohr magnetons was obtained for the solid. This is lower than the values reported for NiX_4^{-2} anions,[2] and for tetrahedral $((C_6H_5)_3PO)_2NiX_2$ and $((C_6H_5)_3AsO)_2NiX_2$ complexes,[3] but higher than the values reported for the tetrahedral $((C_6H_5)_3P)_2NiX_2$ compounds.[4] Diiodobis-(pyridine)-nickel(II) was prepared by refluxing a mixture of anhydrous nickel(II) iodide and pyridine for eight hours. The excess pyridine was decanted and the solid product washed with boiling alcohol. A light green solid, diiodotetra-(pyridine)-nickel(II) separated from the alcohol on cooling. This was heated at 110° in an Abderhalden apparatus until the uniform dark green product was obtained. *Anal.* Calcd. for $C_{10}H_{10}I_2NiN_2$: Ni, 12.47; I, 53.92. Found: Ni, 12.65; I, 53.56.

Diiodobis-(β-picoline)-nickel(II) was prepared in a similar manner, except that the reaction mixture was refluxed only 30 minutes. After decanting the excess picoline, the light green tetrapicoline complex was washed with petroleum ether before converting to the dark green bispicoline complex by heating. The tetrahedral configuration of this compound is indicated by the similarity of its infrared spectra with that of the corresponding blue cobalt(II) complex and by its visible and near infrared spectra in KBr and benzene solution. The absorption maxima in benzene are 405 mμ (2040), 462(2060), 585(300), 925(90) and 1000(100). A value of 3.21 was obtained for the magnetic moment of the solid. *Anal.* Calcd. for $C_{12}H_{14}I_2NiN_2$: C, 28.90; H, 2.83. Found: C, 28.27; H, 3.47.

It was expected that steric effects would prevent halogen bridging in the bis complexes of α-picoline with $NiCl_2$ and $NiBr_2$. This appears to be the case. These compounds are dark blue, indicating that they are tetrahedral. Solid dichlorobis-(α-picoline)-nickel(II) absorbs at 555 and 950 mμ (weak) and has a magnetic moment of 3.3. Solid dibromobis-(α-picoline)-nickel(II) absorbs at 562 and 950 mμ (weak) and has a magnetic moment of 3.35. The dibromo complex was prepared by refluxing anhydrous nickel bromide in an excess of α-picoline for 30 minutes. The excess ligand was removed under vacuum and the product washed several times with petroleum ether and then dried over phosphoric anhydride. It could not be recrystallized as it decomposes in the usual solvents. *Anal.* Calcd. for $C_{12}H_{14}Br_2NiN_2$: Ni, 14.26; C, 35.60; H, 3.47. Found: Ni, 14.15; C, 34.36; H, 4.17. The dichloro compound was prepared by adding equivalent portions of nickel(II) chloride hexahydrate and α-picoline to absolute ethanol. After considerable stirring the mixture was placed in a vacuum desiccator over sulfuric acid for several

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(1) Supported in part under AEC Contract AT(11-1)-38, Radiation Laboratory of the University of Notre Dame.

(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(3) D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5774 (1960).

(4) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *ibid.*, **83**, 344 (1961).

days. The product was washed several times with petroleum ether. It could not be recrystallized because of decomposition in the usual solvents. *Anal.* Calcd. for $C_{12}H_{14}Cl_2NiN_2$: Ni, 18.58; Cl, 22.45. Found: Ni, 18.70; Cl, 24.17.

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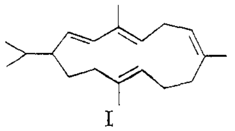
RECEIVED MARCH 21, 1962

CEMBRENE, A 14-MEMBERED RING DITERPENE HYDROCARBON[1]

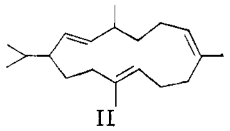
Sir:

Cembrene (I) is a crystalline diterpene hydrocarbon ($C_{20}H_{32}$, mol. wt. 272 (mass spectrum[2]), m.p. 59–60°, $[\alpha]^{23}\mathrm{D}$ + 238° (*c* 1.13, chf.)) first isolated by Haagen-Smit, Wang and Mirov,[3] from the oleoresin of *Pinus albicaulis* and subsequently found to occur in exudate of many other pine trees.[4,5] Cembrene,[6] upon catalytic hydrogenation over Pd/C in ethyl acetate, yielded a liquid saturated octahydro derivative ($C_{20}H_{40}$, mol. wt. 280 (mass spectrum[2])), establishing the presence of four double bonds and one ring in the starting material (I). The ultraviolet and infrared spectra of cembrene, $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 17,000), $\nu_{\max}^{\mathrm{CS_2}}$ 1660 (w), 1640 (w), 967 (s), 840 (m), 811 (m) cm.$^{-1}$, indicated the presence of a conjugated diene as well as *trans*-disubstituted and trisubstituted double bonds. From the n.m.r. spectrum[7] (quantitative) of cembrene, it was determined that there was an isopropyl group attached to a saturated carbon (two doublets centered at 9.09 and 9.20 p.p.m., 6 protons), two methyl groups on double bonds (8.47 and 8.38 p.p.m.), and one methyl group on a conjugated diene (8.20 p.p.m.). The presence of five vinyl protons was established by a broad absorption band between 3.80 and 5.30 p.p.m. containing a sharp doublet at 3.80 and 4.07 p.p.m. equal to one proton. The low field position of this doublet characteristic of a proton on a *trans*-disubstituted double bond further indicated that the bond was part of the conjugated diene system.

Reduction of the conjugated diene system of I with lithium in liquid ammonia gave a mixture of dihydrocembrenes,[8] whose ultraviolet spectrum possessed no maximum above 205 mμ, and which consisted of two compounds in the ratio of 85:15 (g.l.c., silicone, 215°). The infrared absorption at 973 cm.$^{-1}$ of the major component (II) indicated the continued presence of the *trans*-disubstituted double bond and the n.m.r. spectrum showed the presence of four vinyl protons.



I

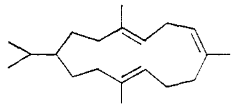


II

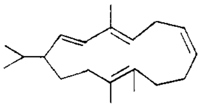
Ozonization of II and treatment with hydrogen peroxide gave 2-isopropyl-5-oxocaproic, 2-methylglutaric, and levulinic acids (isolated as methyl esters by gas-liquid chromatography, silicone, 110°). These three acids account for all twenty carbon atoms of the cembrene molecule. Since all are bifunctional, and since cembrene possesses but one ring, the dihydro derivative and therefore cembrene must contain a fourteen carbon ring. There are eight possible structures for the lithium-liquid ammonia produced dihydrocembrene (II) which could yield these three degradation products.

Ozonization of cembrene and treatment with hydrogen peroxide gave acetic, malonic, 2-isopropyl-5-oxocaproic, and levulinic acids (isolated as methyl esters by gas-liquid chromatography, silicone, 110°). When the ozonide was treated with sodium iodide, then *p*-nitrophenylhydrazine, the *p*-nitrophenylosazone of pyruvaldehyde was isolated. The absence of 2-methylglutaric acid and the appearance of malonic and pyruvic acid moieties permits placement of the olefinic bond which was reduced to form dihydrocembrene II and suggests eight related structures for cembrene.

Catalytic hydrogenation of cembrene over 5% Pd/C in ethyl acetate gave a mixture of three dihydrocembrenes (gas-liquid chromatography, silicone, 200°). The major component III (no maximum in the ultraviolet; n.m.r., 3 vinyl protons; no 970 cm.$^{-1}$ band) was different from dihydrocembrene II and was formed by the hydrogenation of the *trans*-disubstituted double bond of the conjugated diene.



III



IV

Ozonization of III and treatment with hydrogen peroxide gave rise to approximately equal amounts of neutral and acidic materials. The major components of the latter were levulinic and malonic acids.

The eight possible structures of cembrene may be reduced to four by elimination of all structures not containing a *trans*-disubstituted double bond as part of the conjugated system. Two of the remaining four structures also may be eliminated, since the product from their dihydrogenation would not yield levulinic and malonic acids upon ozonization. The two remaining structures are isoprenoid I and the non-isoprenoid IV.

Hydroboration of III, then oxidation, gave a triol mixture V, whose n.m.r. spectrum showed a broad peak at 6.28 p.p.m. corresponding to three protons attached to carbon atoms bearing hydroxyl groups. Acetylation of V with acetic anhydride and sodium acetate at 145° gave the triacetate VI whose n.m.r. spectrum showed a broad band at 5.20 p.p.m. corresponding to three protons at-

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[1] This work was supported in part by Grant No. 14526, National Science Foundation.

[2] We are indebted to Dr. D. P. Stevenson of Shell Development Company for all the mass spectral data quoted in this work.

[3] A. J. Haagen-Smit, T. H. Wang, and N. T. Mirov, *J. Am. Pharm. Assn., Sci. Ed.*, **40**, 557 (1951).

[4] N. T. Mirov, "Composition of Gum Turpentines of Pines," Technical Bulletin No. 1239, U. S. Department of Agriculture, June, 1961.

[5] W. G. Dauben and C. Ashcraft, unpublished observations.

[6] We are indebted to Dr. N. T. Mirov for the supply of oleoresin.

[7] All chemical shifts are quoted in reference to the τ scale.

[8] Satisfactory analyses were obtained for all new compounds.