factors to be considered. The data are not extensive enough to permit speculation.

Spectra of the 2 : 1 Complexes.—The spectrum of the magnetically normal compound dibromobis(2,6-lutidine N-oxide)copper(II) is typical of a great many four-coordinate copper(II) complexes with distorted structures lying somewhere between a square-coplanar arrangement and a tetrahedron.[20] Even though the magnetic properties of the 2:1 complex of 4-picoline N-oxide with copper bromide suggests a di- or polymeric structure, the spectrum of the complex is very similar to that of the magnetically normal and presumably monomeric compound. It is unfortunate that all solvents which will dissolve these compounds also decompose them, thus ruling out the use of conductivity or dipole moment measurements.

At least three structures must be considered before an assignment for the 2:1 complexes can be made. On the basis of the structure exhibited by $[Cu(C_5H_5NO)Cl_2]_2$ and the similarity of the spectra of the compounds, the planar *cis* or *trans* structures with the fifth and/or sixth coordination positions filled by chloride ions from an adjacent molecule may be less likely than a distorted tetrahedral arrangement of nearest neighbor ligand atoms. A positive structural assignment must be deferred until the completion of some single-crystal X-ray studies which are underway in Professor Morrow's laboratory.

Mechanism for Spin–Spin Coupling.—The data collected in this study support the earlier proposal that the spin–spin coupling in binuclear pyridine N-oxide complexes of copper halides occurs by a mechanism which operates through the orbitals of the bridging oxygen atoms.[6] The effect of the substituent is most easily seen in terms of a valence bond model for the substituted pyridine N-oxides. The methyl group donates electron density by resonance to the nitrogen atom adjacent to the bridging oxygen atom, thereby reducing the positive charge on the nitrogen atom which in turn diminishes the importance of canonical forms with nitrogen–oxygen double bonds. In this way the methyl groups enhance the electron density in the p_z orbitals of the bridging oxygen atoms and stabilize the singlet state of the dimeric molecules in the same manner that has been described for a series of binuclear Schiff's base complexes of copper(II).[11]

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[20] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 272; C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Inc., New York, N. Y., 1962, p 286.

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Titanium(IV) Chelates Containing Binegative Ligands

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The reaction of titanium(IV) alkoxides in 1:1 stoichiometry with 2-methyl-2,4-pentanediol, pyrocatechol, salicylic acid, or P,P′-diphenylmethylenediphosphinic acid yields chelates of the form $Ti(BB)(OR)_2$, where BB represents the binegative bidentate ligands involved and R is ethyl or isopropyl. A similar reaction with 1,3-propanediol does not produce $Ti(OC_3H_6O)(OR)_2$, but instead $Ti(OC_3H_6O)_2$ and $Ti(OR)_4$ are recovered. The $Ti(BB)(OR)_2$ derivatives are all associated in solution. Replacement of the alkoxy groups with acetylacetonate groups in the pyrocatecholate derivative gives the monomeric mixed chelate $[Ti(o\text{-}C_6H_4O_2)(C_5H_7O_2)_2]$. P,P′-Diphenylmethylenediphosphinic acid was prepared *via* the reaction of diisopropyl phenylphosphonite with methylene iodide.

In connection with our polymer studies we had a need for compounds of the type $Ti(BB)X_2$ in which BB represents a doubly charged chelating group and X is a readily replaced anion. Examination of the literature failed to reveal any good candidates for our purposes, so we undertook the synthesis of a few compounds of this type. As the reactive group X we selected alkoxides and for the chelating agent pyrocatechol, salicylic acid, and P,P′-diphenylmethylenediphosphinic acid. We also repeated the reaction of $Ti(OC_2H_5)_4$ with 2-methyl-2,4-pentanediol, the only alkoxy derivative of the $Ti(BB)X_2$ type which we found described in the literature,[1] and attempted to make $Ti[O(CH_2)_3O][OCH(CH_3)_2]_2$.

Experimental Section

The sensitivity of many of the titanium compounds to moisture required the use of carefully dried solvents and reagents as well as manipulation in the absence of moist air.

Materials.—Technical grade 2-methyl-2,4-pentanediol (Matheson Coleman and Bell) was dried by refluxing with a small amount of sodium and then vacuum distilled, $n^{25}\text{D}$ 1.4266 (lit.[2] $n^{17}\text{D}$ 1.4298).

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[1] A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, **81**, 2663 (1959).

[2] D. I. Duveen and J. Kenyon, *J. Chem. Soc.*, 1451 (1936).

By a similar procedure 1,3-propanediol (Eastman Kodak Co.) was purified, $n^{24}{}_D$ 1.4391 (lit.[3] $n^{20}{}_D$ 1.4389). Pyrocatechol and salicylic acid (Eastman Kodak Co.) were sublimed *in vacuo* prior to use. Titanium tetraethoxide was prepared according to the procedure of Bradley, *et al.*[4] Titanium tetraisopropoxide (E. I. du Pont de Nemours and Co.) was redistilled, bp 78–79.5° (16 torr). All solvents except chlorinated and acidic ones were distilled from sodium under nitrogen prior to use. Chloroform was distilled from P_2O_5 and alcohols from the corresponding titanium alkoxide.

P,P′-Diphenylmethylenediphosphinic Acid.—To 186 g (0.82 mole) of diisopropyl phenylphosphonite contained in a reaction flask which was attached to a distillation apparatus was quickly added 22.2 ml (0.28 mole) of methylene iodide. The reaction flask was then immersed in an oil bath preheated to 175°. After 1 hr the distillation of isopropyl iodide was completed, and the reaction mixture was refluxed overnight with concentrated hydrochloric acid. The aqueous layer was removed by azeotropic distillation with benzene. Cooling then yielded a colorless crystalline solid which could be recrystallized from water or ethanol, mp 233–234°. *Anal.* Calcd for $C_{13}H_{14}O_4P_2$: C, 52.71; H, 4.76; P, 20.92; neut equiv, 148.1. Found: C, 52.72; H, 5.08; P, 20.39; neut equiv, 146.6. The average yield was 43%.

$Ti[(CH_3)_2C(O)CH_2CH(O)CH_3](OC_2H_5)_2$.—This chelate was prepared by the published procedure[1] with stoichiometric amounts of $Ti(OC_2H_5)_4$ and the diol. Three fractions which differed from each other in viscosity and refractive index were obtained by fractional distillation. The middle fraction, bp 136–144° (0.06 torr) and $n^{25}{}_D$ 1.5100 (lit.[1] 1.517), represented about 60% of the total distillate. *Anal.* Calcd for $C_{10}H_{22}O_4Ti$: C, 47.25; H, 8.72; Ti, 18.8; formula wt, 254. Found: C, 46.56; H, 8.56; Ti, 19.2; mol wt, 780 (ebulliometry in benzene).

$Ti[O(CH_2)_3O]_2$.—To a benzene solution of 23.3 g (0.082 mole) of $Ti[OCH(CH_3)_2]_4$ was gradually added with stirring 6.24 g (0.082 mole) of $HO(CH_2)_3OH$ over a period of 15 min. The liberated $(CH_3)_2CHOH$ was azeotroped off with benzene at atmospheric pressure. After all of the solvent had been removed *in vacuo*, a slightly yellow, exceedingly viscous liquid remained. Distillation gave 10.6 g (91% yield) of moisture-sensitive liquid, bp 51–56° (0.1–0.2 torr), identified by its infrared spectrum as $Ti[OCH(CH_3)_2]_4$.[5] The solid residue in the distillation flask was extracted with benzene, and a nearly white, infusible solid was obtained. *Anal.* Calcd for $C_6H_{12}O_4Ti$: C, 36.75; H, 6.17; Ti, 24.4. Found: C, 37.61; H, 6.66; Ti, 24.9.

$Ti(o\text{-}C_6H_4O_2)(OC_2H_5)_2$.—To a solution of 23.5 g (0.103 mole) of $Ti(OC_2H_5)_4$ in 100 ml of benzene was added over a period of 25 min 11.3 g (0.103 mole) of pyrocatechol. Immediately a dark red solution formed. The solvent and liberated alcohol were removed at reduced pressure. The dark red, solid residue melted at 85–90°; yield 96%. *Anal.* Calcd for $C_{10}H_{14}O_4Ti$: C, 48.80; H, 5.73; Ti, 19.46. Found: C, 48.44; H, 5.73; Ti, 19.9.

$Ti(o\text{-}C_6H_4O_2)[OCH(CH_3)_2]_2$.—To 18.1 g (0.064 mole) of $Ti[OCH(CH_3)_2]_4$ in 200 ml of benzene was slowly added 7.0 g (0.064 mole) of pyrocatechol. Solvent and alcohol were removed at reduced pressure from the red solution. Recrystallization from dry benzene gave 16.2 g (yield 93%) of yellow-orange crystals which formed a dark red liquid above their mp, 112–114°. *Anal.* Calcd for $C_{12}H_{18}O_4Ti$: C, 52.57; H, 6.62; Ti, 17.47; formula wt, 274.2. Found: C, 52.80; H, 6.40; Ti, 18.1; mol wt, 770 (ebulliometry in benzene) and 685 (cryoscopy in benzene).

$Ti[o\text{-}C_6H_4(O)COO](OC_2H_5)_2$.—To 12.4 g (0.054 mole) of $Ti(OC_2H_5)_4$ in benzene was gradually added with stirring 7.46 g (0.054 mole) of salicylic acid. Volatiles were removed from the orange solution *in vacuo*. Washing with petroleum ether (bp 30–60°) left 14.3 g (yield 97%) of yellow solid melting at 166–168° with apparent decomposition. *Anal.* Calcd for $C_{11}H_{14}O_5Ti$: C, 48.19; H, 5.15; Ti, 17.47; formula wt, 274. Found: C, 48.54; H, 5.48; Ti, 17.35; mol wt, 1420 (ebulliometry in benzene).

$Ti[o\text{-}C_6H_4(O)COO][OCH(CH_3)_2]_2$.—This compound was prepared similarly to $Ti[o\text{-}C_6H_4(O)COO](OC_2H_5)_2$. The orange-yellow product melted at 166–173° with apparent decomposition, yield 84%. *Anal.* Calcd for $C_{13}H_{18}O_5Ti$: C, 51.67; H, 6.00; Ti, 15.9; formula wt, 302.2. Found: C, 50.78, 50.75; H, 5.87, 6.30; Ti, 15.5, 16.1; mol wt, 2850 (Mechrolab thermoelectric molecular weight apparatus, chloroform).

$Ti[C_6H_5P(O)_2CH_2P(O)_2C_6H_5][OCH(CH_3)_2]_2$.—In an inert atmosphere 5.79 g (0.02 mole) of $C_6H_5P(O)(OH)CH_2P(O)(OH)C_6H_5$ was added to a solution of 5.56 g (0.02 mole) of $Ti[OCH(CH_3)_2]_4$ in 175 ml of benzene. After approximately 50 ml of solvent was removed *in vacuo*, a white, crystalline precipitate gradually formed. It was removed, washed with petroleum ether, and dried *in vacuo*. Additional product was obtained upon removal of solvent; yield 96%. The colorless product did not melt up to 440°. *Anal.* Calcd for $C_{19}H_{26}O_6P_2Ti$: C, 49.58; H, 5.70; P, 13.46; Ti, 10.4; formula wt, 460.3. Found: C, 49.39; H, 5.75; P, 12.92; Ti, 10.7; mol wt, 4640 (ebulliometry in chloroform).

$Ti[C_6H_5P(O)_2CH_2P(O)_2C_6H_5]_2$.—To 2.75 g (0.097 mole) of $Ti[OCH(CH_3)_2]_4$ in 150 ml of toluene was added 5.73 g (0.0194 mole) of $C_6H_5P(O)(OH)CH_2P(O)(OH)C_6H_5$. After reflux for 5 hr the reaction mixture was filtered, and 5.69 g of crude product was obtained. Upon extraction with isopropyl alcohol and petroleum ether there remained 2.87 g (yield 47%) of white solid. *Anal.* Calcd for $C_{26}H_{24}O_8P_4Ti$: C, 49.08; H, 3.80; Ti, 7.5. Found: C, 48.65; H, 4.56; Ti, 7.5.

$Ti(o\text{-}C_6H_4O_2)(CH_3COCHCOCH_3)_2$.—To 8.76 g (0.032 mole) of $Ti(o\text{-}C_6H_4O_2)[OCH(CH_3)_2]_2$ in 200 ml of benzene was added 6.46 g (0.065 mole) of freshly distilled 2,4-pentanedione. After most of the solvent and liberated alcohol were removed by distillation, a brown, crystalline precipitate formed in the residual 60 ml of solution. Removal and washing with petroleum ether yielded 7.2 g of product, and an additional 3.1 g was obtained from the mother liquor for a total yield of 91%. The solid, mp 222–223°, appeared quite stable in air. *Anal.* Calcd for $C_{16}H_{18}O_6Ti$: C, 54.25; H, 5.12; Ti, 13.52; formula wt, 354.2. Found: C, 54.65; H, 5.31; Ti, 13.9; mol wt, 350 (thermoelectric method in benzene).

Infrared Spectra.—Infrared spectra were determined with a Perkin-Elmer Model 221 instrument employing a sodium chloride prism and a Perkin-Elmer Model 337 grating spectrophotometer.

Molecular Weight.—The ebullioscopic molecular weight measurements were determined with the equipment as described by Dimbat and Stross.[6] A Mechrolab thermoelectric molecular weight apparatus was used in some cases. The molecular weights were calculated from data obtained in the 0.2–1.5% concentration range. Comparative slope methods were employed, and in general good straight lines passing through or reasonably near the origin were obtained.

Discussion

The limited amount of work that we have done with aliphatic diols by and large confirms the observations in the literature. Thus, the compound with the composition $Ti[(CH_3)_2C(O)CH_2CH(O)CH_3](OC_2H_5)_2$ is a viscous liquid with a molecular weight indicative of association,[1] and the compound with the composition $Ti[O(CH_2)_3O]_2$ is an infusible solid insoluble in common organic solvents.[7] We, however, found it necessary to fractionate the crude product corresponding to the former because the distillate was not uniform. The resulting purified product had a molecular weight corresponding to a trimer, not a dimer as reported earlier.[1] The latter, previously made from stoichiometric

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[3] A. F. Gallaugher and H. Hibbert, *J. Am. Chem. Soc.*, **58**, 813 (1936).

[4] D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.*, 721 (1955).

[5] J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *Anal. Chem.*, **25**, 1720 (1953).

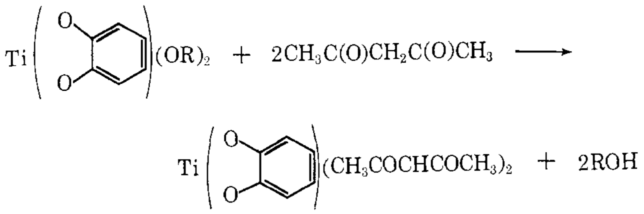
[6] M. Dimbat and F. H. Stross, *ibid.*, **29**, 1517 (1957).

[7] A. Deluzarche and M. Brini, *Bull. Soc. Chim. France*, **3**, 537 (1961).

amounts of reactants, was isolated along with $Ti[OCH(CH_3)_2]_4$ when we attempted to work up the viscous liquid obtained from the reaction of $Ti[OCH(CH_3)_2]_4$ with 1,3-propanediol in 1:1 stoichiometry. It, therefore, appears that the desired product, $Ti[O(CH_2)_3O][OCH(CH_3)_2]_2$, if it forms at all, disproportionates quite readily, and we suspect that the discrepancy in molecular weight between our work and the earlier work with $Ti[(CH_3)_2C(O)CH_2CH(O)CH_3](OC_2H_5)_2$ may also be due to disproportionation.

Because these 1:1 titanium derivatives of aliphatic diols proved not extremely stable, we turned to aromatic chelating groups. There have been some reports of titanium derivatives of pyrocatechol[7,8] but no indication of the type $Ti(o\text{-}C_6H_4O_2)X_2$. In fact, the reaction of $TiCl_4$ with pyrocatechol in 1:1 stoichiometry is reported to yield $Ti_2(o\text{-}C_6H_4O_2)_3Cl_2$.[7] Both $Ti(OC_2H_5)_4$ and $Ti[OCH(CH_3)_2]_4$ react with pyrocatechol in 1:1 molar ratio to give the desired composition, $Ti(o\text{-}C_6H_4O_2)(OR)_2$. The products are air-sensitive, benzene- and chloroform-soluble, yellow-orange to red solids which can be kept unchanged only in sealed glass vessels. Exposure to air converts them to dark brownish red infusible solids which do not have a definite composition. Molecular weight studies indicate that these pyrocatechol derivatives are associated in chloroform or benzene solution with a degree of polymerization between 2 and 3. Consequently, they do not have a cross-linked polymer structure such as suggested for $Ti_2(o\text{-}C_6H_4O_2)_3Cl_2$.[7]

These 1:1 pyrocatechol chelates of titanium react readily with 2,4-pentanedione to form the mixed chelate $[Ti(o\text{-}C_6H_4O_2)(CH_3COCHCOCH_3)_2]$



Its molecular weight in chloroform corresponds to a monomer, and the absence of conductivity in its chloroform solution indicates it is not a salt.

There also have been no earlier reports on the isolation of 1:1 derivatives of titanium(IV) and salicylic acid. A continuous variations study in aqueous solution[9] gave evidence for only a 1:3 derivative although both 1:3 and 1:2 derivatives have been isolated.[8,10]

Like pyrocatechol, salicylic acid reacts with $Ti(OC_2H_5)_4$ or $Ti[OCH(CH_3)_2]_4$ in 1:1 stoichiometry to yield a 1:1 derivative, in this case $Ti[o\text{-}C_6H_4(COO)(O)](OR)_2$. The products isolated are orange solids for which the molecular weight data indicate association, but to a greater extent than for the corresponding pyrocatechol derivatives. This is perhaps due to the presence of more oxygen atoms in the chelating ligand. Examination of the C=O absorption region in the infrared spectra led to neither support nor refutation of such a possibility.

A new chelating agent, P,P′-diphenylmethylenediphosphinic acid, was also synthesized as a part of this study. It was readily made by a Michaelis–Arbuzov type of reaction between $C_6H_5P[OCH(CH_3)_2]_2$ and methylene iodide followed by acid hydrolysis of the diester produced

$$2C_6H_5P[OCH(CH_3)_2]_2 + CH_2I_2 \longrightarrow \underset{\text{I}}{C_6H_5P(O)[OCH(CH_3)_2]CH_2P(O)[OCH(CH_3)_2]C_6H_5} + 2(CH_3)_2CHI$$

$$\text{I} + 2H_2O \xrightarrow{H^+} C_6H_5P(O)(OH)CH_2P(O)(OH)C_6H_5 + 2(CH_3)_2CHOH$$

A 1:1 or a 1:2 derivative resulted from the reaction of $Ti[OCH(CH_3)_2]_4$ with this acid, depending on the stoichiometry used. Both products are colorless solids which do not melt up to 400°; however, darkening occurs above 300° in a closed capillary. Hydrolysis in hot water does not remove the chelate group in $Ti[C_6H_5P(O)_2CH_2P(O)_2C_6H_5][OCH(CH_3)_2]_2$, but the hydrolysate does not have a definite composition. The failure of these chelates to melt is somewhat surprising but may be explained by cross linking involving P=O groups of the chelate. This explanation is borne out by their low solubility and molecular weights in excess of 1000. Unfortunately, a complex infrared spectrum does not permit an unequivocal assignment of the P=O stretching frequencies.[11]

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(8) A. Rosenheim and O. Sorge, *Ber.*, **53**, 932 (1920).

(9) N. K. Dutt and N. Goswami, *Z. Anorg. Allgem. Chem.*, **298**, 258 (1959).

(10) A. Rosenheim, R. Schnabel, and R. Bilecki, *Ber.*, **48**, 447 (1915).

(11) Note Added in Proof.—After our manuscript was accepted for publication, we became aware of the work by Varma and Mehrotra [L. D. Varma and R. C. Mehrotra, *J. Prakt. Chem.*, **10**, 247 (1960)] on the reaction of titanium alkoxides with α-hydroxy carboxylic acids including salicylic acid through its criticism by Yamada and co-workers [S. Yamada, K. Kusunoki, and W. Sakai, *J. Electrochem. Soc. Japan*, **33**, 166 (1965)]. Our observations confirm and extend those of Varma and Mehrotra. During the same period a paper mentioning the preparation of P,P′-diphenylmethylenediphosphinic acid became available to us [P. Mastalerz, *Roczniki Chem.*, **39**, 1129 (1965)].