

hr and -23° for 16 hr gave a 46% yield from **5a** of all-trans squalene **6**.²⁵

As an example of the use of synthon **5a** in an unsymmetrical fashion, it was treated with 1 mol of dihydropyran in the presence of *p*-toluenesulfonic acid to give **5c** (45%), together with **5d** and recovered **5a** (separated on silica gel using benzene with increasing amounts of ethyl acetate). Treatment of **5c** with carbon tetrabromide-triphenylphosphine led to **5e**. *trans,trans*-Farnesyltributylphosphonium boronide²² was alkylated with **5e** and the product was reduced with lithium in methylamine and tetrahydrofuran (-78° , 4 hr) to give a 40% yield of **7** from **5e**. Synthesis of **7** enables unsymmetrical coupling and introduction of specific labeled fragments. It is clear that suitable manipulation also allows differential substitution of the two methylene groups of the C₁₀ unit.

(25) A quantitative yield of thiourea clathrate was obtained from **6** which was identical [ir, nmr, and gc (20% FFAP, 6 ft \times 1/4 in.)] with an authentic sample of all-trans-squalene. The cis-trans ratio of allylic methyl groups was 3:1.

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An Unusual Five-Coordinate Complex of Copper(II)

Sir:

It is well known that the nitrite anion (NO₂⁻) is capable of bonding to transition metals in several different ways. It may bond through the nitrogen to give the well-known nitro complexes or through one of the oxygens to give the less common nitrito complexes. The anion may also function as a bridging ligand coordinating through the nitrogen and one of the oxygens.^{1,2} Recently the nitrite anion has been shown to also be capable of acting as a bidentate ligand, coordinating through the two oxygens.³ This last mode of coordination is by far the least common. There are, however, no reports of the nitrite anion coordinating in two different ways in the same monomeric complex. It is the purpose of this communication to report such a complex.

We have previously shown that the ligand *N,N'*-ethylenedimorpholine (EDM) (C₁₀H₂₀N₂O₂) has extreme steric requirements.⁴⁻⁶ During the course of our investigation of the coordination chemistry of this ligand, we prepared the Co(II), Ni(II), and Cu(II) nitrite complexes of EDM. It was anticipated that all three complexes would have an octahedral coordination geometry obtained from two bidentate nitrite groups and one bidentate EDM ligand, as has been found

with other sterically demanding nitrogen ligands, tetramethylethylenediamine, quinoline, and α -picoline.³

All three complexes were prepared according to the general method of Goodgame and Hitchman and had the stoichiometry M(NO₂)₂(EDM).^{3,7} The cobalt and nickel complexes were shown to be isomorphous through their X-ray powder patterns. Both of the complexes are nonelectrolytes in methylene chloride solution. The electronic spectra of both complexes can be readily interpreted on the basis of an octahedral model. The nickel complex has absorption bands at 9250 cm⁻¹ (ϵ 7.5), 15,150 (ϵ 14), and 25,000 (ϵ 42). The cobalt complex has absorptions at 8350 cm⁻¹ (ϵ 16), 18250 (ϵ 81), and 20,200 (ϵ 65). The magnetic moments of the complexes, determined by the method of Evans, are also consistent with an octahedral coordination geometry.⁸ That of the nickel complex is 3.26 BM while that of the cobalt complex is 4.67 BM. This latter value is somewhat lower than is normally found for octahedral cobalt(II) complexes, but several authors have reported magnetic moments in this range.⁹ The infrared spectra of the two complexes show nitrite absorptions at 850, 1175, and 1300 cm⁻¹. These infrared absorptions are compatible only with nitrite acting as a bidentate ligand bonding through the two oxygens.^{3,10} Thus, cobalt and nickel nitrite complexes of EDM have been assigned the anticipated octahedral coordination geometry.

The copper complex, however, is not isomorphous with the cobalt and nickel complexes. It is a nonconducting monomer in methylene chloride and chloroform solutions. The magnetic moment of 1.95 BM at 305°K is in the range that is normally found for Cu(II) complexes, where there are no magnetic interactions between neighboring ions. The electronic spectrum consists of one band in the near-infrared and visible regions at 14,100 cm⁻¹ (ϵ 197). This band is asymmetric to lower energies. It is very probable that there is more than one absorption band within this envelope, but it is not possible to resolve them. The infrared spectrum of the complex has nitrite absorptions at 1375, 1350, 1290, and 1175 cm⁻¹. There are also shoulders at about 860 and 830 cm⁻¹ which are probably due to nitrite absorptions, but they cannot be assigned with certainty because they appear as shoulders on more intense ligand bands. The bands at 1290, 1175, and 860 cm⁻¹ are the same as those found for nitrite in a bidentate environment. The appearance of NO₂⁻ absorptions at 1375, 1350, and 830 cm⁻¹ indicates that nitrite is also functioning in a manner other than as a bidentate ligand in the complex. The positions of these "extra bands" is most compatible with nitrite behaving as a monodentate ligand coordinating through nitrogen.¹⁰

Thus, with one bidentate nitrite and one monodentate nitrite as well as one EDM molecule in the coordina-

(1) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959).

(2) K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 80, 4817 (1958).

(3) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 4, 721 (1965).

(4) A. L. Lott II and P. G. Rasmussen, *J. Amer. Chem. Soc.*, 91, 6502 (1969).

(5) A. L. Lott II and P. G. Rasmussen, *J. Inorg. Nucl. Chem.*, 32, 101 (1970).

(6) A picture of the ligand may be found in either ref 4 or 5.

(7) Satisfactory elemental analyses (C, H, and N) and molecular weights were obtained for all new complexes. They were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(8) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(9) (a) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsey, and S. Y. Tyree, *J. Amer. Chem. Soc.*, 83, 3770 (1961); (b) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 388 (1959); (c) E. Banister and F. A. Cotton, *ibid.*, 2276 (1960).

(10) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, pp 151-155; (b) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 3, 1389 (1964).

tion sphere a five-coordinate complex must be postulated. The two limiting pentacoordinate geometries for Cu(II) and other transition metals are the trigonal bipyramid and the square pyramid. Trigonal-bipyramidal Cu(II) complexes normally exhibit two distinct bands in the near-infrared and visible regions.¹¹ Square-pyramidal Cu(II) complexes, on the other hand, show only one asymmetric absorption maximum in this region.¹² On this basis, a structure based on a square pyramid seems to be indicated.

- (11) (a) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964);
 (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 41 (1966).
 (12) W. K. Musker and M. S. Hussain, *ibid.*, **8**, 528 (1969).

A crystal structure of this unusual compound was undertaken to provide the details about the coordination polyhedron. Preliminary results show that the deep emerald green crystals belong to one of the monoclinic space groups *Cc* or *C2/c*. The lattice parameters are $a = 12.01$, $b = 7.29$, $c = 17.72$ Å, and $\beta = 95.4^\circ$. The density of 1.54 g/cm³ is in agreement with the 1.53 g/cm³ calculated for four molecules per unit cell. Complete details of the structure will be reported at a later date.

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Additions and Corrections

Chemistry of the Gentamicins. II. Stereochemistry and Synthesis of Gentosamine. Total Structure of Gentamicin A [*J. Amer. Chem. Soc.*, **92**, 1697 (1970)]. By HUBERT MAEHR and CARL P. SCHAFFNER, Rutgers University, The State University of New Jersey, Institute of Microbiology, New Brunswick, New Jersey 08903.

The date of receipt of this manuscript by the journal was September 6, 1969, instead of October 23, 1969.

Bridged Polycyclic Compounds. LXII. Stereochemistry and Mechanisms of Electrophilic Addition to Cyclopropane Rings [*J. Amer. Chem. Soc.*, **92**, 4013 (1970)]. By STANLEY J. CRISTOL, WENDEL Y. LIM, and ALAN R. DAHL, Department of Chemistry, University of Colorado, Boulder, Colorado 80302

On page 4016, column 1, the last line should read (in part): $J_{56syn} = 6.5$, $J_{56anti} = 8.5$. . .

Page 4016, column 2, line 24 ff should read: (3 H, s, methoxy H), 7.28 (1 H, quartet, C-6 probably *anti* H), ~6.68 (2 H, m, C-5H and C-6 probably *syn* H); $J_{15} = 7$, $J_{43} = 2.5$; $J_{56anti?} = 9.5$, $J_{anti6syn} = 18$, $J_{56syn?}$ indeterminate due to peak overlap.

On page 4017, line 8, column 2, *syn* should be replaced by *anti*.

The Nature of So-Called Titanocene, (C₁₀H₁₀Ti)₂ [*J. Amer. Chem. Soc.*, **92**, 6182 (1970)]. By HANS H. BRINTZINGER and JOHN E. BERCAW, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104.

The first line in the three right-hand columns of Table I, which reads: 372 . . . 1 . . . (C₁₀H₁₀TiCH₃)₂⁺, should be replaced by the following two lines: 386 . . . < 1 . . . (C₁₀H₁₀TiCH₃)₂⁺ and 372 . . . 1 . . . C₁₀H₁₀Ti)₂CH₃H⁺. We are grateful to Dr. C. D. Schmulbach for pointing this error out to us.

Homoallylic Participation. III. The Effect of a 2-Methyl Group [*J. Amer. Chem. Soc.*, **92**, 7101 (1970)]. By ROGER S. MACOMBER, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

On page 7102, in the fifth line under Table I, and on page 7103, in the line under Scheme II, α should read β .

In Figure 1, the abscissa legend should read $\ln ([IIIb]_0/[IIIb]_t)$.

On page 7104, column 2, line 6, the value quoted from ref 1b for the acetolysis of X should read 2.8×10^{-5} .

Conformations of Six-Membered Ring Phosphorus Heterocycles. Preferred Axial Orientation of Methyl on Phosphorus in a Six-Membered Ring *tert*-Butyl-Substituted Methylphosphonite [*J. Amer. Chem. Soc.*, **93**, 797 (1971)]. By WESLEY G. BENTRUDE, K. C. YEE, RICHARD D. BERTRAND, and DAVID M. GRANT, Department of Chemistry, University of Utah, Salt Lake Lake City, Utah 84112.

The ³¹P chemical shifts -161.6 and -185.2 assigned in Table I to the trans and cis isomers, respectively, of 1a should be interchanged.

The Use of Carbon-13 Nuclear Magnetic Resonance (Cmr) Spectroscopy in Biosynthetic Studies. Incorporation of Carboxyl and Methyl Carbon-13 Labeled Acetates into Cephalosporin C [*J. Amer. Chem. Soc.*, **93**, 2337 (1971)]. By NORBERT NEUSS, CLAUDE H. NASH, and PAUL A. LEMKE, Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana, and JOHN B. GRUTZNER Department of Chemistry, Purdue University, Lafayette, Indiana.

The assignments of C-3 and C-4 in Tables I and II should be reversed. Further work has now established the assignments for compound IV as C-3, 73.9; C-4, 75.8; C-4', 69.8.