C–P–C bond angle is 98.9°.[12] In IIa, strain in the bicyclic structure would be minimized if the bond angles in the rings were near the tetrahedral angle. Such an increase in the C–P–C bond angle would give rise to an increase in s character in the P–C bond and consequently larger P–C–H coupling would be realized.

The downfield proton chemical shift observed upon oxidation of IIa as well as the small differences in proton chemical shift among IIb, IIc, and IId parallels that found previously for the polycyclic phosphite compounds IIIa, IIIb, and IIIc.[7]

The P^{31} n.m.r. data in Table II lend further support for the formulation of IIa, IIb, and IIc.[13] The chemical shifts observed for the bicyclic compounds IIIa, IIIb, and IIIc, also shown in Table II, are seen to agree well with the shifts obtained for the analogous phosphorus atom in IIa, IIb, and IIc. Moreover, the P^{31} chemical shift for the "phosphine" phosphorus in IIc lies close to the value observed for the analogous phosphorus nucleus in IIa. If the sulfur atom were bound to the "phosphine" phosphorus, a negative chemical shift such as that observed for trimethylphosphine sulfide (−48.0 p.p.m.)[14] would be expected.

TABLE II

P^{31} CHEMICAL SHIFTS IN DIMETHYL SULFOXIDE (P.P.M. *vs.* 85% AQUEOUS H_3PO_4)

Compound	$P^{31}[P\text{-}(CH_2)_3]$	$P^{31}[PO_3]$	J_{PCH}, c.p.s.	J_{POCH}, c.p.s.
$C_3H_6O_3P_2$ (IIa)	+67.0	−90.0	8.9	2.6
$C_3H_6O_5P_2$ (IIb)	− 6.4	+18.1	...[a]	...[a]
$C_3H_6O_3P_2S$ (IIc)	+ 70.6	−51.8	Not observed	
$C_3H_6O_4P_2S$ (IId)[b]				
$C_5H_9O_3P$ (IIIa)		−91.5[c]		2[c]
$C_5H_9O_4P$ (IIIb)		+7.9[c]		7[c]
$C_5H_9O_3PS$ (IIIc)		−57.4[c]		6[c]

[a] Values are indistinguishable within experimental error. [b] Insufficient solubility. [c] J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

Because of the high symmetry of these molecules the infrared spectra contain relatively few bands. Weak fundamental C–H stretching and deformation bands at 2920 and 1429 cm.$^{-1}$, respectively, are evident in the spectrum of IIa, while strong bands at 1046 and 963 cm.$^{-1}$ may be due to C—O and P—O modes. The spectrum of IIb is similar except for a strong phosphate P═O mode at 1325 cm.$^{-1}$ and a strong phosphine P═O mode at 1220 cm.$^{-1}$, while IIc exhibits a strong band at 807 cm.$^{-1}$ which may be due to the P═S stretching frequency. In IId the P═S and P═O modes appear at 807 and 1215 cm.$^{-1}$, respectively. Complete assignment of these and other bands will be the subject of a future publication.

It is not surprising that the 1,4-dioxo compound (IIb) is formed rather easily. Various attempts to prepare a monooxo compound of IIa have thus far been unsuccessful. In view of the apparent ease with which trialkylphosphine sulfides are produced under fusion conditions,[15] it is worthy of note that only a monosulfide is formed wherein the sulfur atom is bonded to the "phosphite" phosphorus even in the presence of a 100% excess of sulfur.

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[12] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).

[13] The long-range P^{31}–P^{31} coupling constants will be discussed elsewhere.

[14] M. L. Nielsen, J. V. Pustinger, Jr., and J. Strobel, *J. Chem. Eng. Data*, **9**, 167 (1964).

[15] R. A. Zingaro and R. E. McGlothlin, *ibid.*, **8**, 226 (1963).

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Preparation and Properties of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II)

BY J. A. BERTRAND AND ROY I. KAPLAN

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Several complexes containing both methoxide and β-dicarbonylate ions have been reported[1,2]; these can be represented by the general formula $MA(OCH_3)(CH_3OH)_x$. A beryllium complex,[1] with A representing the anion of 3-nitro-2,4-pentanedione and $x = 0$, was reported to have a molecular weight corresponding to a mixture of dimeric and trimeric species; cobalt(II) complexes,[2] with A representing the anion of salicylaldehyde, *o*-hydroxyacetophenone, or 2,4-pentanedione and $x = 1$, were found to have much higher associations. Complexes of nickel(II) and magnesium(II),[2] prepared by the same method used for cobalt(II), were analogous to the cobalt(II) complexes; however, copper(II) complexes prepared by the same method did not separate from solution as large crystals as did the other complexes, the solids did not lose weight on heating, and analyses indicated a formula similar to the beryllium complex. We have investigated the copper(II) complex of 2,4-pentanedione further and report here the results of those investigations.

Experimental

Preparation of Di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II).—A 1.8-g. (0.007 mole) sample of bis(2,4-pentanedionato)copper(II) was dissolved in 350 ml. of refluxing methanol and 0.39 g. (0.007 mole) of potassium hydroxide was added dropwise to the refluxing solution. The solution was refluxed for 2 hr. and filtered while hot. The compound was obtained as a violet, microcrystalline solid.

Anal. Calcd. for $C_6H_{10}O_3Cu$: C, 37.2; H, 5.6. Found: C, 37.1; H, 5.3.

The compound is soluble in acetonitrile, chloroform, dichloromethane, nitromethane, and pyridine.

Spectral Measurements.—Spectra in the visible and ultraviolet were obtained with a Carey Model 14 spectrophotometer. Chloroform was used as solvent.

The infrared spectrum was obtained with a Perkin-Elmer

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[1] R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1189 (1963).

[2] J. A. Bertrand and D. Caine, *J. Am. Chem. Soc.*, **86**, 2298 (1964).

Model 21 spectrophotometer. Both a Nujol mull and a chloroform solution were run.

Molecular Weight Determination.—The molecular weight was obtained with a Mechrolab vapor pressure osmometer at 37° using chloroform as solvent. Values of 439, 403, and 395 were obtained for 0.0125, 0.0250, and 0.0500 F solutions, respectively.

Magnetic Susceptibility Determination.—The magnetic susceptibility of the compound was measured at room temperature with a Gouy balance. The uncorrected molar susceptibility was 215×10^{-6} c.g.s. unit and was independent of field strength.

Results and Discussion

The copper(II) complex differs from the other divalent transition metal complexes both in formulation and in association. Although the other complexes were highly associated, the degree of association varying with concentration, the copper(II) compound was essentially dimeric in chloroform at all concentrations.

The magnetic moment of the compound was calculated using the expression $\mu_{\text{eff}} = 2.84[\chi_{\text{m}}^{\text{cor}} - N\alpha)T]^{1/2}$. A diamagnetic correction of -78×10^{-6} was used and a value of $N\alpha$ of 60×10^{-6} per copper ion was assumed. The value obtained, 0.75 B.M., was considerably below the value for one unpaired electron.

The dimeric nature, the low magnetic moment, and the tendency of copper(II) to achieve four-coordination suggest that there are bridging groups present in the compound. Although there is no bridging by the oxygens of bis(2,4-pentanedionato)copper(II),[3] such bridging is known to exist in trimeric bis(2,4-pentanedionato)nickel(II)[4] and in tetrameric bis(2,4-pentanedionato)cobalt(II)[5] and it is possible that the 2,4-pentanedione oxygens are the bridging groups in this compound. The methoxide ion often acts as a bridging group,[6] and it seems more probable that the methoxides are the bridging groups; however, there is some evidence of both bridging and terminal methoxides in copper(II) methoxide.[7]

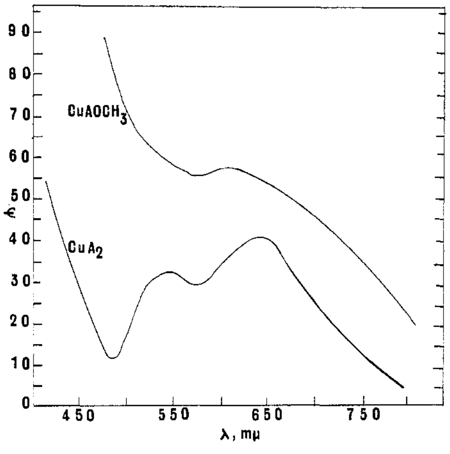


Figure 1.—Visible spectra of di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II) and bis(2,4-pentanedionato)copper(II). Extinction coefficients are based on formula weight per copper(II) ion.

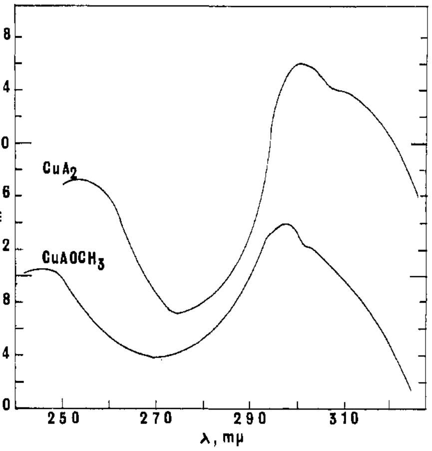


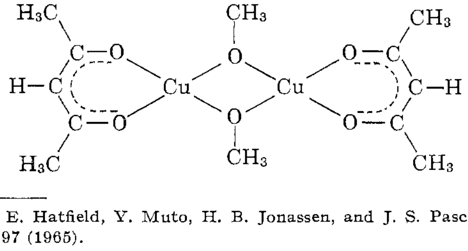
Figure 2.—Ultraviolet spectra of di-μ-methoxo-bis(2,4-pentanedionato)dicopper(II) and bis(2,4-pentanedionato)copper(II). Extinction coefficients are based on formula weight per copper(II) ion.

It has been suggested[6] that bridging methoxides have a carbon–oxygen stretching below 1040 cm.$^{-1}$, while terminal methoxides absorb above 1060 cm.$^{-1}$. Since only one band, at 1018 cm.$^{-1}$, is observed in this region for the copper(II) complex, it appears that only bridging methoxides are present in this compound.

Assuming that the dimer is bridged by the methoxides, there is still the possibility of at least two different structures for the complex; either a planar or a tetrahedral arrangement could exist. A series of complexes with bridging oxygens, $[\mathrm{Cu(pyO)Cl_2}]_2$ (where pyO represents various substituted pyridine N-oxides), has been reported,[8] and all of the compounds have low magnetic moments; the structure of the compound containing unsubstituted pyridine N-oxide has been determined[9] and shows a distorted tetrahedral arrangement around the copper. However, a large number of copper(II) compounds, including bis(2,4-pentanedionato)copper(II),[3] are square-planar.

The visible spectrum of this complex, Figure 1, consists of a broad band centered around 16,000 cm.$^{-1}$. The absorption is similar in wave length and in intensity to that of bis(2,4-pentanedionato)copper(II) and other square-planar complexes of copper(II); tetrahedral complexes of copper(II) with oxygen donors do not absorb in the visible region, the weaker crystal field causing a shift to lower energy.[10]

Although other structures may be possible, the experimental evidence is consistent with a planar, dimeric structure



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(3) H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **C4**, 43 (1953).

(4) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

(5) F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964).

(6) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

(7) C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).

(8) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(9) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 272.

It is possible to rule out, in addition to tetrahedral structures and structures containing bridging carbonyl oxygens, any structure which would significantly alter the chelate ring since the ultraviolet spectrum of this compound and that of bis(2,4-pentanedionato)copper(II), Figure 2, are identical except for intensity (the bands of the methoxide complex are approximately half as intense); the infrared absorptions of the 2,4-pentanedionato group are similar in the two compounds.

An X-ray investigation to confirm the suggested structure had been planned, but numerous attempts to obtain single crystals of the compound have failed.

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Identification of Organosilanols by Nuclear Magnetic Resonance Spectroscopy

BY J. F. HAMPTON, C. W. LACEFIELD, AND J. F. HYDE

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In a recent communication,[1] Chapman and King described the use of dimethyl sulfoxide (DMSO) in identifying alcohols by nuclear magnetic resonance spectroscopy. The classification of alcohols was determined by the degree of hydroxyl proton splitting. In a related investigation we have examined the n.m.r. spectra of various organosilanols in DMSO, and our preliminary results are reported herein.

In contrast to spectra recorded in common n.m.r. solvents sharp hydroxyl proton absorptions were obtained for all organosilanols examined. In addition, the use of DMSO allowed us to observe the first reported case of spin–spin splitting of the hydroxyl proton with an organosilanol. These latter two observations are illustrated by the spectra of diphenylsilanol determined in carbon tetrachloride (Figure 1) and DMSO (Figure 2). Thus, in DMSO solutions, extensive hydrogen bonding of the silanols to the solvent reduces the rate of proton exchange sufficiently to permit these observations. Hydroxyl proton exchange in DMSO is slow relative to the reciprocal of the doublet splitting ($1/J_{\mathrm{HSiOH}}$), but is still rapid enough to permit complete hydroxyl proton–deuterium exchange in phenyldimethylsilanol in less than a minute.

Application of DMSO has proved extremely useful in the analysis of silanols in the presence of other hydroxyl-containing species. The n.m.r. spectrum of a DMSO solution of a mixture of organosilanols, *t*-butyl alcohol, and water shows separate, sharp, resolvable hydroxyl proton absorptions for all species (Figure 3). Table I lists the various proton resonance assignments for this n.m.r. spectrum.

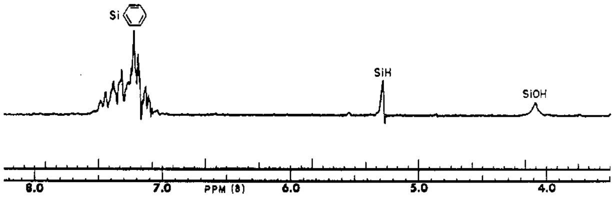

Figure 1.—N.m.r. spectrum of diphenylsilanol in carbon tetrachloride.

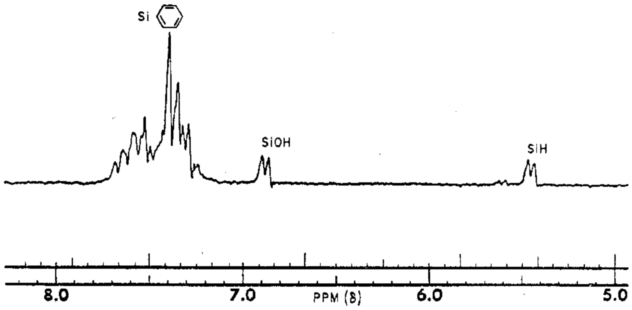

Figure 2.—N.m.r. spectrum of diphenylsilanol in DMSO showing the spin–spin splitting of the hydroxyl proton and silane proton resonances.

TABLE I

PROTON RESONANCE ASSIGNMENTS FOR FIGURE 3

Ref. no.	Assignment
1	$(\mathit{CH}_3)_4\mathrm{Si}$
2	$(\mathit{CH}_3)_3\mathrm{SiOH}$
3	$\mathrm{C_6H_5}(\mathit{CH}_3)_2\mathrm{SiOH}$
4	$(\mathrm{C_6H_5})_2\mathit{CH}_3\mathrm{SiOH}$
5	$(\mathit{CH}_3)_3\mathrm{COH}$
6	DMSO–C^{13} high-field side band
7	High-field spinning side band
8	High-field spinning side band
9	$(\mathit{CH}_3)_2\mathrm{SO}$
10	Low-field spinning side band
11	Low-field spinning side band
12	$\mathit{H}_2\mathrm{O}$
13	DMSO–C^{13} low-field side band
14	$(\mathrm{CH_3})_3\mathrm{CO}\mathit{H}$
15	$(\mathrm{CH_3})_3\mathrm{SiO}\mathit{H}$
16	$\mathrm{C_6H_5(CH_3)_2SiO}\mathit{H}$
17	$(\mathrm{C_6H_5})_2\mathrm{CH_3SiO}\mathit{H}$
18	$(\mathrm{C_6H_5})_3\mathrm{SiO}\mathit{H}$
19	$(\mathrm{C}_6\mathit{H}_5)_3\mathrm{SiOH}$, $(\mathrm{C}_6\mathit{H}_5)_2\mathrm{CH_3SiOH}$, $\mathrm{C}_6\mathit{H}_5(\mathrm{CH_3})_2\mathrm{SiOH}$

Chemical shift data for the hydroxyl proton resonance of a large variety of organosilicon compounds are given in Table II.

At present, the advantages of using DMSO in n.m.r. studies of organosilanols include: (1) sharp, resolved hydroxyl absorptions, (2) independence of concentration on the position of the silanol hydroxyl resonance below 20 mole %, (3) use as a criterion of purity, (4) quantitative analysis of silanol, alcohol, and water mixtures, (5) observation of hydroxyl spin–spin splitting of silanols, (6) resolution of unequivalent hydroxyl absorptions in polyhydroxyorganosilicon com-

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[1] O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).