also unsuccessful, the product obtained being an ill-defined air-sensitive yellow solid the infrared spectrum of which (Table I) indicated the presence of two phosphorus atoms and one nitrogen atom in the coordination sphere of Mo. Thus the product might be formulated as $Mo(CO)_3(NPN)_2$, in which one NPN is bonded to Mo through a nitrogen and a phosphorus, while the other NPN is bonded only through phosphorus. This behavior is not inconsistent with the following observations.

(1) Though $M(CO)_3(amine)_3$ complexes are well known, they have been reported only for primary and cyclic amines.

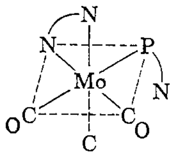
(2) $Mo(CO)_4(en)$[4] and $Mo(CO)_4(tmen)$[4] are air stable, but the corresponding complex of the bulky teen[4] decomposes *in vacuo* despite the order of electron-releasing ability of substituent groups in the ligands, $H < CH_3 < C_2H_5$.

(3) While triphenylphosphine replaces tmen from $Mo(CO)_4(tmen)$ to give, finally, *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$ as the only product, less sterically demanding ligands, *e.g.*, trimethyl phosphite, give spectroscopic evidence for the formation of the "mixed" trisubstituted complexes, $Mo(CO)_3(tmen)(phosphite)$.[5]

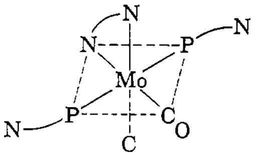
(4) Amine basicities vary in the order: diethylamine > triethylamine > cyclohexylamine. $Mo(CO)_3(phen)(amine)$ complexes have been reported[3b] for diethylamine and cyclohexylamine, but the bulkier triethylamine does not form an analogous complex.

These results should indicate that the relatively weaker bonding of amines than phosphines in such complexes renders amine–metal bond formation quite sensitive to steric factors; attempted correlations of ligand bonding properties to ligand basicity in such systems should be made with extreme caution.

Reactions of $Mo(CO)_4(phen)$ with the ligands give complexes in which one or two carbonyls are replaced only by phosphorus atoms of the ligands (Table I), the remaining carbonyls being mutually *cis*, again as demonstrated by comparison of the infrared spectra of the derivatives and "model" complexes. The failure of the amines to coordinate is not surprising, since such coordination would involve the replacement of a carbonyl *trans* to the phen ligand (II) rather than *trans* to the more strongly π-accepting phosphorus, as is possible with the coordination of two independent ligands (III).

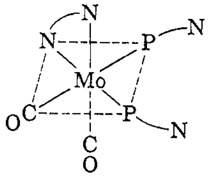


II



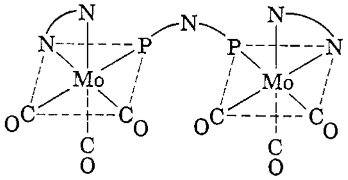
III

The similarity of the carbonyl stretching spectra for the derivatives reported here and the "model" complexes, in which the two phosphorus atoms are believed to be *trans* to one another,[3a] supports similar stereochemistry. Somewhat higher carbonyl stretching frequencies would be expected were the phosphorus atoms *cis* since, for the *trans* isomer, each carbonyl is also *trans* to a phen nitrogen (III) while, for the *cis* isomer, one carbonyl is *trans* to a nitrogen and the other is *trans* to a phosphorus (IV).



IV

The ligand PNP functions as a bridging group to give the first example of a "mixed" binuclear derivative of the group VIb metal carbonyls. Bridging occurs through the two phosphorus atoms, the amine being uncoordinated (V), as determined by chemical analysis and infrared spectral data (Table I).



V

Acknowledgment.—Support of this research by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Contribution from the Istituto di Chimica,
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Basic Zinc Dialkylphosphinothioates

By S. Meriani, G. Nardin, and A. Ripamonti

Received April 21, 1967

Interest in the structure and properties of coordination polymers, involving bridging phosphinate groups,[1] prompted us to examine the ability of the thio derivatives of phosphinic acid to act as bridging groups between tetrahedral metal ions. During the course of an investigation of the polymeric nature of Zn(II) and Co(II) dialkylphosphinothioates of stoichiometry $M(R_2PSO)_2$ (where M = Zn(II), Co(II) and $R = C_2H_5$, n-C_4H_9), we obtained under certain conditions zinc salts which display basic properties.

Running different preparations, using the metal acetates and the dialkylphosphinothioic acids in ethanol, we obtained the normal salts, which are polymers in noncoordinating solvents and in the solid state.[2] The normal salts $Co(R_2PSO)_2$ could also be obtained using cobalt carbonate, whereas the reaction with zinc car-

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(1) V. Crescenzi, V. Giancotti, and A. Ripamonti, *J. Am. Chem. Soc.*, **87**, 391 (1965); V. Giancotti and A. Ripamonti, *Chim. Ind.* (Milan), **48**, 1065 (1966); F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Commun.*, 19 (1967).

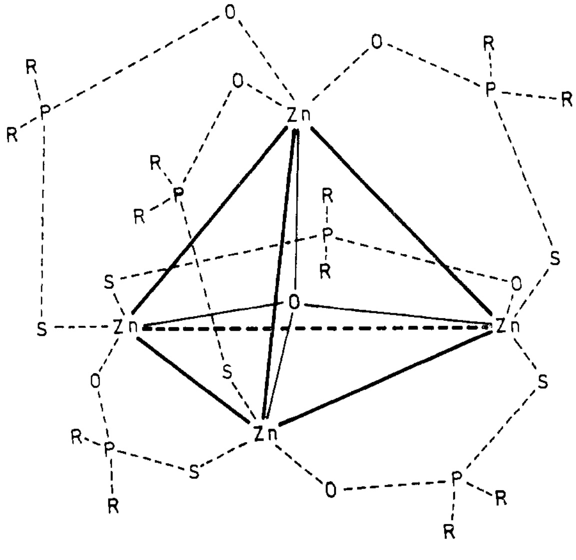
(2) A. Ciana, S. Meriani, and A. Ripamonti, submitted for publication.

bonate yielded basic compounds. The elemental analyses of both ethyl and *n*-butyl basic salts indicate a ratio between zinc atoms and phosphinothioate groups of 1:1.5 against the 1:2 ratio of the normal salts. The neutralization equivalents, obtained by aqueous acid–base titrations of the hydrolyzed salts, are one-half the molecular weights, measured by vapor pressure osmometry with benzene as solvent. These data lead to the formula $Zn_4O(R_2PSO)_6$, which suggests a molecular geometry similar to that established for basic beryllium acetate[3] and basic zinc acetate[4] and to that recently proposed for basic zinc O,O-dialkylphosphorodithioates.[5]

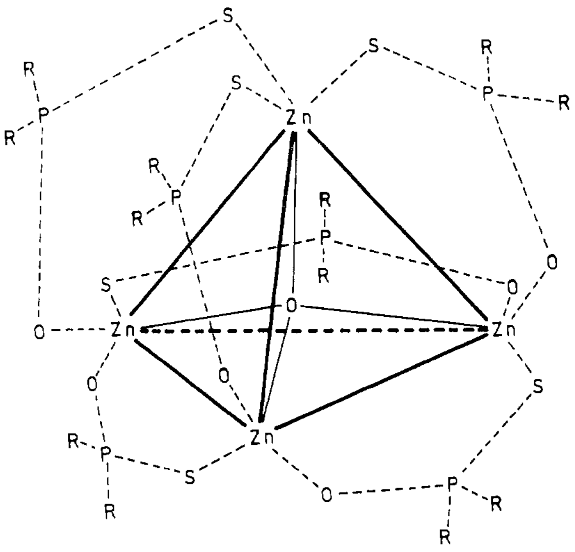
Convincing evidence for the molecular geometry was derived from a single-crystal X-ray diffraction study of the basic zinc di-*n*-butylphosphinothioate.

The trigonal crystals have lattice parameters a_r = 12.47 A and α = 84.0° and the following dimensions of the hexagonal cell: a_{hex} = 16.64 A and c_{hex} = 23.75 A. The flotation-measured density of 1.27 g cm^{-3} compares favorably with the calculated density of 1.254 g cm^{-3} for three molecules per hexagonal cell.

The systematic absences, $-h + k - l = 3n + 1$, and the Laue symmetry indicate R3 and R$\bar{3}$ as possible space groups. The latter space group demands that the molecule possess a threefold inversion axis. Since this symmetry is impossible for a molecule containing four zinc atoms, the probable space group is R3, which demands a threefold molecular symmetry. This implies a central oxygen atom surrounded tetrahedrally by four zinc atoms, a phosphinothioate group lying beyond each edge of the tetrahedron in a closely similar way with that proposed for O,O-dialkylphosphorodithioates.[5] However, assuming an ordered structure, two molecular formulas I and II with threefold symmetry are possible because of the asymmetry of the dialkylphosphinothioate group.



I



II

In I the top zinc atom, located on the threefold axis, has four oxygen atoms as nearest neighbors—the central one and the three of different phosphinothioate groups—whereas the other three zinc atoms are surrounded by two oxygen and two sulfur atoms. In II the top zinc atom is surrounded by the central oxygen atom and the three sulfur atoms of different phosphinothioate groups, whereas one sulfur and three oxygen atoms are arranged around the other three zinc atoms.

It should be noted that, on the basis of present data, one cannot exclude the possibility of a disordered structure. In fact, molecules with randomly oriented dialkylphosphinothioate groups might occur indiscriminately in the crystal so that it appears to contain molecules with threefold symmetry. Nevertheless the name which should be assigned to the basic zinc dialkylphosphinothioates is μ_4-oxo-hexa-μ-dialkylphosphinothioate-tetrazinc. Therefore these compounds belong to the class of tetranuclear complexes with a four-coordinated central oxygen atom, as, for example, $Be_4O(CH_3COO)_6$,[3] $Zn_4O(CH_3COO)_6$,[4] $Mg_4OBr_6(C_4H_{10}O)_4$,[6] $Co_4O(C(CH_3)_3COO)_6$,[7] $Cu_4OCl_6((C_6H_5)_3PO)_4$.[8]

Experimental Section

Diethylphosphinothioic acid, $(C_2H_5)_2PSOH$, and di-*n*-butylphosphinothioic acid, $(C_4H_9)_2PSOH$, were prepared by methods described in the literature.[9] Other chemicals were reagent grade and were used without further purification.

Molecular weight measurements were carried out with a Mechrolab vapor pressure osmometer at 37° in benzene at the concentrations stated in parentheses.

The titration of the basic salts was accomplished, after extensive hydrolysis in boiling water, either by the direct method or by back titration an excess of 0.01 *N* sulfuric acid with standard base. Brom phenol blue was used as the indicator.

Crystallographic data were obtained from precession photographs taken with Cu Kα radiation.

Preparation of Basic Zinc Di-*n*-butylphosphinothioate.— $(C_4H_9)_2PSOH$ (3.95 g, 0.020 mole) was dissolved in 40 ml of

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[3] L. Pauling and J. Sherman, *Proc. Natl. Acad. Sci. U. S.*, **20**, 340 (1934).

[4] H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, **27**, 112 (1954).

[5] A. J. Burn and G. W. Smith, *J. Chem. Soc.*, 394 (1965).

[6] G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

[7] A. B. Blake, *Chem. Commun.*, 569 (1966).

[8] J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).

[9] E. Müller "Methoden der Organischen Chemie," Vol. XII, Part 1, Georg Thieme Verlag, Stuttgart, 1963, pp 212, 268.

absolute ethanol, and $ZnCO_3$ (1.7 g, 0.014 mole) was added to the warm solution. The reaction mixture was refluxed with stirring for a 6–8-hr period and then filtered to remove any unreacted carbonate. The filtrate was cooled down to 0° until a product crystallized; this generally happened after cooling overnight. The solid was filtered, washed with ethanol, and then allowed to dry in air; yield, 1.8 g; mp 104°. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of the mother liquor. The compound is soluble in benzene, carbon tetrachloride, and chloroform and insoluble in cold water.

Anal. Calcd mol wt for $Zn_4O((C_4H_9)_2PSO)_6$: 1437.0. Found (0.86, 1.00, 2.05 g/100 ml): 1387, 1428, 1443. Calcd neut equiv: 718.5. Found: 710.9, 720.1. Calcd for $Zn_4C_{48}H_{108}P_6S_6O_7$: Zn, 18.19; C, 40.11; H, 7.57. Found: Zn, 18.02; C, 41.14; H, 7.88.

Preparation of Basic Zinc Diethylphosphinothioate.—The same procedure given for the *n*-butyl derivative, using $(C_2H_5)_2PSOH$ (0.99 g, 0.007 mole) and $ZnCO_3$ (0.6 g, 0.005 mole), yielded 0.4 g of product, mp 273°. The compound is soluble in benzene, carbon tetrachloride, and chloroform and is insoluble in cold water.

Anal. Calcd mol wt for $Zn_4O((C_2H_5)_2PSO)_6$: 1100.4. Found (0.80, 1.30, 2.00 g/100 ml): 1052, 1030, 1081. Calcd neut equiv: 550.19. Found: 554.8, 540.4. Calcd for $Zn_4C_{24}H_{60}P_6S_6O_7$: Zn, 23.76; C, 26.19; H, 5.49. Found: Zn, 23.70; C, 25.60; H, 5.20.

Acknowledgment.—This research was supported in part by the Italian "Consiglio Nazionale delle Ricerche."

CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY,
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Clarification of Discrepancies in the Characterization of Lanthanum Series Complexes of 2,2,6,6-Tetramethyl-3,5-heptanedione

BY J. E. SCHWARBERG, D. R. GERE, R. E. SIEVERS, AND K. J. EISENTRAUT

Received May 15, 1967

Large discrepancies have been observed in the properties of lanthanum series chelates with the anion of 2,2,6,6-tetramethyl-3,5-heptanedione prepared by the methods of Hammond, *et al.*,[1] and Eisentraut and Sievers.[2] We have repeated the synthesis of the Er(thd)$_3$ complex[3] using both procedures. The product isolated using the Hammond method is an adduct with N,N-dimethylformamide, DMF, and the one isolated from the procedure in ref 2, an unsolvated complex with the formula Ln(thd)$_3$. DMF adducts resulted also when the unsolvated chelates were recrystallized from DMF. These Ln(thd)$_3$·DMF adducts have the properties of the products obtained by Hammond. Table I lists the melting points of complexes prepared by the various methods.

TABLE I
MELTING POINTS OF LANTHANUM SERIES COMPLEXES PREPARED BY VARIOUS PROCEDURES

Metal	Mp,[2] °C	Mp,[1] °C	Mp, °C, DMF adducts, this work[b]
Er	179–181	153–154	153–154
Sm	195.5–198.5	143–144	146.5–147.5
Ho	180–182.5	154–155	151.5–154.5
La	238–248[a]	148–149	118–235[c]

[a] Melting point taken in a sealed, evacuated tube. [b] Prepared by recrystallization of the Ln(thd)$_3$ complexes from DMF as described in the Experimental Section. A second sample of the Er(thd)$_3$·DMF adduct was prepared by the method in ref 1; this sample melted within 2° of the value in the table. [c] The melting point of this adduct depended upon the length of time it was exposed to air for removal of excess DMF.

The Ln(thd)$_3$·DMF adducts have not been recognized in the literature, although another DMF adduct of a rare earth β-diketonate, namely, tris(dibenzoylmethanato)(N,N-dimethylformamide)europium(III),[4] has been characterized. Other claims for the existence of thd complexes of various types have also been reported.[5,6] However, adducts of the type Ln(β-diketonate)$_3$·L, where L is a mono- or bidentate ligand with oxygen or nitrogen as the donor, are not uncommon.[4,7–10]

Experimental Section

The preparative methods described in ref 1 and 2 were followed closely to obtain products with properties matching those described in the earlier papers. The Ln(thd)$_3$·DMF adducts were prepared by recrystallization of the unsolvated complexes from hot DMF. The excess DMF was removed using a water aspirator to pull air through a sintered funnel containing the solid for 4 or 5 hr, followed by exposure to air overnight.

Thermogravimetric Analyses.—Ten-milligram samples were used in the Du Pont Model 950 thermogravimetric analyzer. The heating rate was set for 10°/min and the flow of dry helium, measured with a soap bubble flowmeter, was 60 cc/min.

Nmr Spectra.—Proton nmr spectra of carbon tetrachloride solutions were obtained with the Varian Associates Model A-60 spectrometer at the ambient probe temperature. The internal reference was tetramethylsilane.

Infrared Spectra.—The Perkin-Elmer Model 137B Infracord spectrophotometer was used for comparison of spectra for the products isolated from the various synthetic procedures. Samples in the form of mineral oil mulls were held between rock salt plates. Band positions in the 4000–600-cm^{-1} range were accurately measured with the Perkin-Elmer Model 521 grating infrared spectrophotometer for an 11% solution of DMF in CCl_4 and for saturated solutions of Er(thd)$_3$ and Er(thd)$_3$·DMF in CCl_4 using matched 0.025-mm liquid NaCl cells. Below 800 cm^{-1} both erbium complexes were also run as mineral oil mulls with rock salt plates, since C–Cl frequencies in CCl_4 absorbed strongly in some areas of this region.

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(1) G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

(2) K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, **87**, 5254 (1965).

(3) The following abbreviations will be used: Ln = trivalent lanthanum series ions, and thd = the anion of 2,2,6,6-tetramethyl-3,5-heptanedione.

(4) R. G. Charles and R. C. Ohlmann, *J. Inorg. Nucl. Chem.*, **27**, 119 (1965).

(5) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **41**, 157 (1964).

(6) J. S. Brinen, F. Halverson, and J. R. Leto, *ibid.*, **42**, 4213 (1965).

(7) H. Bauer, J. Blanc, and D. L. Ross, *J. Am. Chem. Soc.*, **86**, 5125 (1964).

(8) R. G. Charles and A. Perrotto, *J. Inorg. Nucl. Chem.*, **26**, 373 (1964).

(9) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964).

(10) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).