

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A Spectroscopic Study of the Polymeric Nature of Bis(acetylacetonato)cobalt(II)¹

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Molecular weight measurements and spectroscopic studies of bis(acetylacetonato)cobalt(II) in noncoordinating solvents demonstrate the presence of dimers, trimers, and some still higher oligomers. Comparison of the spectra of CoA₂ at high dilution with the spectrum of the consistently monomeric and tetrahedral bis(dipivaloylmethanido)cobalt(II), Co(DPM)₂, leads to the conclusion that the CoA₂ monomer is also tetrahedral. Comparison of the spectra of the most concentrated solutions of CoA₂ with the spectra of glassy CoA₂, crystalline CoA₂, and CoA₂·2H₂O (or CoA₂·2CH OH) and other considerations leads to the proposal that the oligomers are built up of CoA₂ units, in which the cobalt atoms are in approximately square arrays of oxygen atoms, which combine by further sharing of oxygen atoms. Some arguments are presented to suggest that the tetrahedral configuration of Co(DPM)₂ is 5–20 kcal./mole more stable than the planar one.

Introduction

Although bis(acetylacetonato)cobalt(II), CoA₂, is a common and easily accessible complex of divalent cobalt which has been prepared and studied many times since it was first reported by Gach³ over 60 years ago, its molecular structure and hence also its electronic structure remain uncertain. Its structure, when considered at all, appears generally to have been assumed to be tetrahedral, since such a structure, based on sp³ hybridization of the Co^{II}, is consistent with the known presence of three unpaired electrons. More recently, however, it was suggested that Co^{II} should be capable of forming high-spin square complexes and that various ones containing β-ketoenolate ligands might be examples.⁴

Almost immediately after this suggestion was advanced, however, work in this laboratory⁵ and elsewhere⁶ demonstrated that bis(acetylacetonato)nickel(II) owes its high spin character to the fact that at normal temperatures in the crystalline state and in noncoordinating solvents it is trimeric, each nickel atom being surrounded by an approximately octahedral arrangement of oxygen atoms. It was further shown⁵ that when the methyl groups are replaced by *t*-butyl

groups which are bulky enough to prevent association, the monomeric molecule obtained, bis(dipivaloylmethanido)nickel(II), Ni(DPM)₂, is red, diamagnetic, and presumably planar. It was immediately recognized⁵ that molecular association, not necessarily of the same structural nature, might also play a role in the behavior of CoA₂, thus vitiating the suggestion⁴ that it is a high-spin square complex of Co(II).

This paper reports an investigation, chiefly using visible absorption spectra, into the question of the state of aggregation of CoA₂ under various conditions. Some of the main conclusions to be presented rest upon comparison of CoA₂ spectra with Co(DPM)₂ spectra together with the fact that Co(DPM)₂ has a tetrahedral configuration. This fact was first deduced from space group considerations⁷ and has recently been substantiated by a complete three-dimensional, single crystal X-ray study of the isomorphous Zn(DPM)₂.⁸

Experimental

Preparation of Compounds.—Dipivaloylmethane was prepared according to Fackler and Cotton.⁵ The preparation of Co(DPM)₂ was carried out in a closed apparatus under nitrogen and all solvents were boiled while prepurified nitrogen gas was bubbled through them just prior to use. A solution of 10.0 g. (0.055 mole) of HDPM and 7.87 g. (0.027 mole) of Co(NO₃)₂·6H₂O in 50 ml. of methanol was boiled for 2–3 min. under nitrogen and then stirred during the dropwise addition of 2.16 g. (0.054 mole) of NaOH in 15 ml. of water. A red-pink precipitate formed immediately, but the reaction mixture was refluxed

(1) Supported by the United States Atomic Energy Commission.

(2) (a) Fellow of the Alfred P. Sloan Foundation; (b) N. S. F. Predoctoral Fellow.

(3) F. Gach, *Monatsh.*, **21**, 98 (1900).

(4) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(5) F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **82**, 5005 (1960); **83**, 2818, 3775 (1961).

(6) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

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

(8) F. A. Cotton and J. S. Wood, *Inorg. Chem.*, in press.

and stirred for 2 hr. The methanol was then distilled off in a stream of nitrogen, leaving a red solid in a small amount of water. Petroleum ether ($\sim 70^\circ$) was added and the precipitate dissolved to give a magenta solution. This was separated from the aqueous layer, filtered, and nearly all the petroleum ether was distilled off and replaced by diethyl ether. The quantity of diethyl ether was adjusted to give a solution which appeared to be saturated at the boiling point. This solution was then cooled in an ice bath for 1 hr., and the reddish pink crystals were separated by filtration through a glass frit in a nitrogen atmosphere and quickly transferred to a nitrogen-filled desiccator, where they were kept over Drierite for several days. The color grew paler with drying. The pale pink powder was easily sublimed at 110° under vacuum, giving ruby-red crystals; m.p. (sealed tube) 142° . Yields ran about 80%.

Anal. Calcd. for $\text{C}_{22}\text{H}_{38}\text{O}_4\text{Co}$: C, 62.09; H, 9.02. Found: C, 61.6; H, 8.85.

The strict exclusion of oxygen during the preparation of this compound and while handling it in solution is important, since separation of it from whatever impurities are formed on partial oxidation seems very difficult. The dry solid may be kept in dry air without apparent change for at least 2 months and probably much longer. Since our original report⁷ of this compound, its preparation by a different method has been briefly described by Hammond,⁹ who also notes its sensitivity to oxygen when in solution.

Bis(acetylacetonato)cobalt(II) was prepared by a reported procedure.¹⁰

Molecular Weight Determinations.—Reagent or spectroscopic grade solvents were dried over Drierite, distilled under nitrogen, and stored in tightly closed bottles. Isothermal distillation (isopiestic) measurements were made by the procedure of Signer.¹¹ Cryoscopic determinations were made with a simple apparatus of local design using a Beckmann thermometer and ebullioscopic measurements were made with a locally built Cottrell pump, also using a Beckmann thermometer.

Absorption Spectra.—All data were recorded using a Cary Model 14 spectrophotometer. Solids were examined as mulls in Nujol or hexachlorobutadiene. Cells with path lengths 0.1, 1.0, 5.0, and 10.0 cm. were used to cover an over-all concentration range of about $500\times$.

Magnetic Measurements.—Magnetic susceptibilities were measured using equipment and methods previously described.^{4,12}

Results

Molecular Weight Measurements.—It was considered necessary to be certain that $\text{Co}(\text{DPM})_2$, which occurs as discrete molecules in the crystalline state,^{7,8} is also monomeric in solution. Cryoscopic measurements in benzene and cyclohexane gave the results recorded in Table I which satisfactorily prove the point.

Measurements were made on CoA_2 by three techniques. All the results are collected in Table II. These by no means constitute as complete a study of molecular weight behavior as would be desirable and further studies have been undertaken. However, these data are sufficient for the interpretation of the spectroscopic results which constitute the main aspect of this report. The data in benzene show the dependence of molecular weight on temperature and also show that oligomers higher than trimers will form at the higher concentrations and lower temperatures.

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

(10) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

(11) H. Signer, *Ann.*, **478**, 246 (1930).

(12) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

TABLE I
CRYOSCOPIC MOLECULAR WEIGHT MEASUREMENTS ON $\text{Co}(\text{DPM})_2$

Solvent	Concentration, wt. %	Mol. wt. ^a
Cyclohexane	2.58	421
	2.56	442
	4.90	439
Benzene	1.37	423
	2.80	428

^a Theory for $\text{Co}(\text{DPM})_2$: 426.

In freezing benzene, no concentration dependence of the polymerization number was noted, but the concentration range studied, due to experimental limitations, was rather small. In carbon tetrachloride at $\sim 77^\circ$, concentration dependence is clearly evident. Though scatter in the data is great enough that we eschew drawing dogmatic conclusions, we believe that the correct interpretation is probably that suggested by the curve in Fig. 1. This curve indicates a lower limit in polymerization factor of 1.0 at infinite dilution and an upper limit of ~ 2.0 at this high temperature.

TABLE II
MOLECULAR WEIGHT MEASUREMENTS ON CoA_2

Method	Solvent	Concn., wt. %	Mol. wt.	Polymerization no. ^a
Cryoscopic	Benzene ($\sim 5^\circ$)	1.36	888	3.5
		2.73	865	3.4
		4.05	894	3.5
Isopiestic	Benzene ($\sim 25^\circ$)	1.0	500 \pm 100	1.95 \pm 0.3
Ebullioscopic	Carbon tetrachloride ($\sim 77^\circ$)	2.35	472	1.84
		1.40	410	1.75
		2.60	465	1.81
		3.85	493	1.92
		1.56	447	1.74
		2.96	518	2.02
		4.06	523	2.04
		3.14	496	1.93
		4.35	523	2.02
		0.86	344	1.34
		2.22	445	1.73
3.27	490	1.90		
0.40	334	1.30		
1.15	450	1.75		
2.28	468	1.82		

^a Polymerization number equals observed molecular weight/257.

In general, we believe the molecular weight data suggest and support the following description of the process of molecular association for CoA_2 in noncoordinating solvents: CoA_2 units combine to form dimers, trimers, and still higher oligomers, with probably some special stability to the dimer.¹³ The enthalpy of dissociation per monomer unit seems to be 5–10 kcal./mole based on the data for benzene solutions at 5 and 25° and assuming equal ΔH values and statistically varying ΔS values for successive association steps. This last

(13) X-Ray studies by R. C. Elder of this laboratory on CoA_2 show that the crystals are triclinic with four molecules in the unit cell. This is consistent with the presence of four monomers, two dimers, or one tetramer but eliminates the possibility of a trimeric oligomer unless one makes the rather unlikely assumption that the unit cell contains one monomer and one trimer.

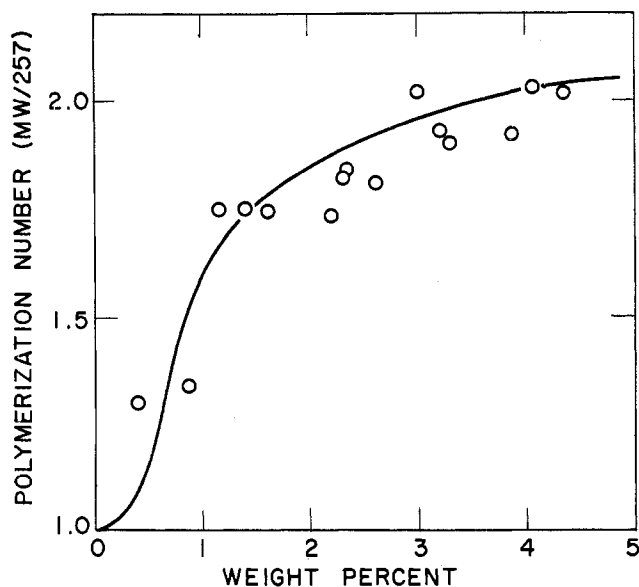


Fig. 1.—The results of ebullioscopic molecular weight measurements on CoA_2 in carbon tetrachloride at $\sim 77^\circ$.

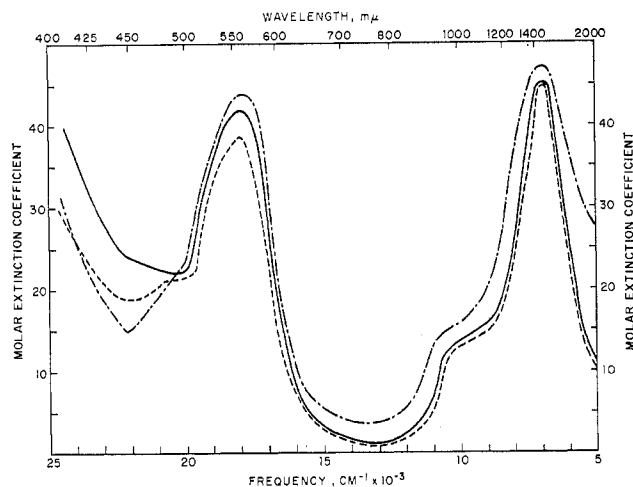


Fig. 2.—Visible and near-infrared spectrum of Co(DPM)_2 : —, 0.141 M in benzene; ---, 0.0141 M in benzene; - · - · -, Nujol mull of crystalline solid. The absorbance scale is arbitrary for the mull spectrum.

result is thus a very crude one, probably valid only to within a factor of 2.

Spectroscopic Measurements.—The spectrum of Co(DPM)_2 in benzene at two concentrations and in crystalline form is shown in Fig. 2. There is no significant dependence of the spectrum on concentration over the range shown and the spectrum of the crystalline compound agrees very well with that of the solution, in view of the changes which frequently occur in a molecular spectrum on changing the phase of the sample. The obvious conclusion is that the tetrahedral, monomeric molecules occurring in the crystal persist, irrespective of concentration, in solutions in noncoordinating solvents.

For CoA_2 , spectral data for solutions of several concentrations in carbon tetrachloride at about 25° are shown in Fig. 3. The deviation from Beer's law is very striking, thus qualitatively supporting the conclusion drawn from the molecular weight measurements that

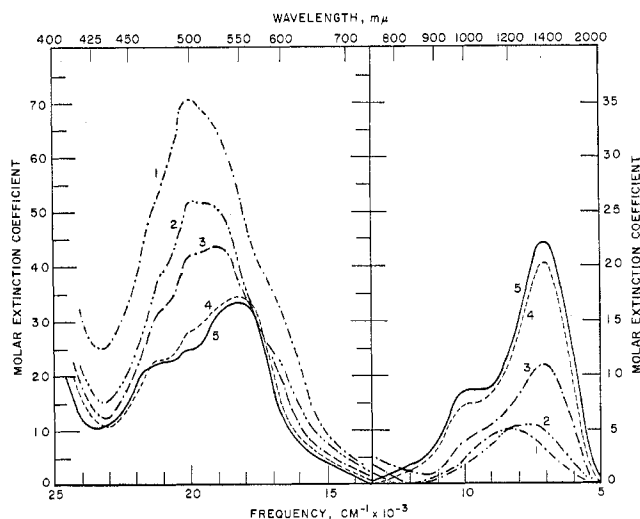


Fig. 3.—Visible and near-infrared spectra of CoA_2 in CCl_4 at various concentrations and $\sim 25^\circ$. The molarity and weight per cent are given in that order for each solution: (1) 0.51, 8.07; (2) 0.158, 2.53; (3) 0.020, 0.32; (4) 0.00238, 0.0383; (5) 0.00117, 0.0187.

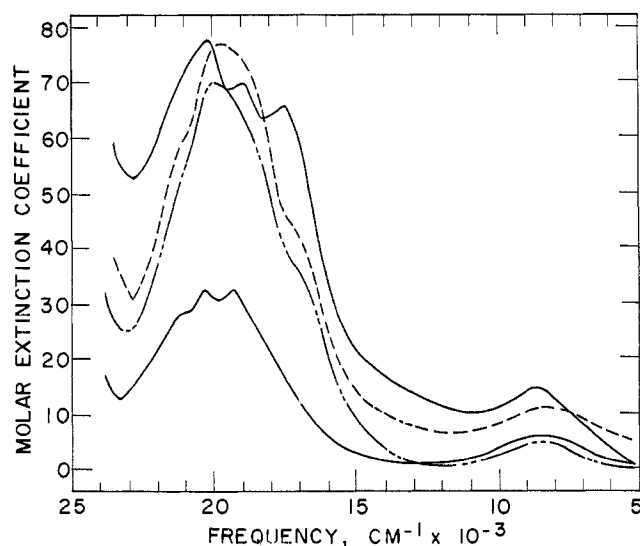


Fig. 4.—Comparison of the spectra of $[\text{Co}(\text{C}_6\text{H}_7\text{O}_2)_2]_2$ in different states of aggregation: — (upper), crystalline solid; ---, glassy solid; - · - · -, 0.5 M solution in carbon tetrachloride; — (lower), $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$, 0.04 M , plus 0.16 M CH_3OH in CHCl_3 .

there is a concentration-dependent molecular association process occurring in noncoordinating solvents. It is also apparent that the spectrum has come very close to reaching a limiting form at the lowest concentrations studied; the apparent differences between the spectra at the two lowest concentrations are just barely outside of the experimental uncertainty. Almost identical results have been obtained using methylene chloride as solvent, thus showing that, except in minor details, the spectral behavior does not depend on the specific solvent so long as it is not a coordinating one.

Spectra of CoA_2 were also run under other conditions. These are shown in Fig. 4. CoA_2 can be fused fairly easily between glass plates. If such a "sandwich" is permitted to cool very slowly, the resulting film of solid appears to be polycrystalline, whereas if it is

cooled as quickly as possible in a stream of cold air, the resulting solid has a distinctly glassy appearance and is at least two-dimensionally isotropic when viewed under a polarizing microscope. The polycrystalline layer appears to consist of randomly oriented minute crystals when viewed in polarized light, but some degree of preferential orientation within the plane of the film cannot be ruled out with complete certainty. Moreover, there is the possibility of preferential orientation of one crystallographic axis perpendicular to the plane of the film. Our observations do not afford any evidence at all regarding this. The spectra recorded on cooled melts of the two types are shown in Fig. 4 along with the spectrum of the most concentrated solution in carbon tetrachloride (same as shown in Fig. 3) and the spectrum of $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoA}_2 \cdot 2\text{CH}_3\text{OH}$, or a mixture of these dissolved in chloroform.

Magnetic Measurements.—For $\text{Co}(\text{DPM})_2$, magnetic susceptibility measurements over the temperature range 75–300°K. give values which can be fitted to a Curie–Weiss equation, $\mu = 2.84[\chi_{\text{Mol}}^{\text{OFT}}(T - \theta)]^{1/2}$, with $\mu = 4.34$ B.M. and $\theta = -10^\circ$. A measurement on a 0.15 *M* benzene solution at room temperature leads to a moment of 4.13 B.M., but this is undoubtedly too low, since the susceptibility of the solution was observed to be decreasing (about 4%/hr.) during the measurement, presumably because of air oxidation of the $\text{Co}(\text{DPM})_2$ to diamagnetic Co^{III} products.

Discussion

The molecular weight, magnetic moment, and spectral data for $\text{Co}(\text{DPM})_2$, together with the crystallographic results,^{7,8} allow us to regard this molecule, both in the crystal and in solution in noncoordinating solvents such as benzene and carbon tetrachloride, as prototypal in its electronic absorption spectrum and magnetic properties for tetrahedral (strictly, D_{2d}) bis(β -keto-enolato)cobalt(II) complexes. With this in mind, we turn to the interpretation of the data for CoA_2 .

First, in carbon tetrachloride, methylene chloride, and presumably other noncoordinating solvents, CoA_2 exists as oligomers which dissociate progressively with decreasing total cobalt concentration. In CCl_4 at $\sim 25^\circ$ nearly complete dissociation is attained at a concentration of ~ 0.03 *M*. In CH_2Cl_2 , essentially complete conversion to the monomer seems to occur between 0.01 and 0.001 *M*.

Second, the CoA_2 monomer is almost certainly tetrahedral in view of the great similarity of the spectrum of $\text{Co}(\text{DPM})_2$ and that of CoA_2 obtained in these very dilute solutions.

Third, comparison of the several spectra shown in Fig. 4 gives some interesting hints, though no entirely unequivocal indications, as to the nature of the oligomers of CoA_2 which arise under various conditions. The spectrum of the most concentrated carbon tetrachloride solution and that of the glassy solid, discounting intensity variations which are without useful significance, are strikingly similar. There are, however, very noticeable differences between these spectra

and that of polycrystalline CoA_2 , mainly in the visible. Because of the possibility of preferred orientation which always arises in polycrystalline samples, it is possible that these differences do not in fact result entirely from differences in molecular structure. We believe that they probably do, however.

Since the molecular weight data indicate that the energy of association of CoA_2 monomers or of monomers with oligomers is fairly low and that this system is not limited to the formation of trimers, we are inclined to believe that association occurs in a manner structurally quite different from that which occurs in forming $(\text{NiA}_2)_3$.¹⁴ While speculation as to the actual structure of the oligomers is somewhat hazardous, chiefly because of the pitfall common to all such "stochastic" deductions of structure, namely, the chance of completely overlooking some general class of possibilities, we wish to suggest a type of structure which seems to satisfy all requirements imposed by the data at hand. Since there seems no likelihood that the structures of the species in solution or in the glassy solid will be determined experimentally in the foreseeable future, speculation on these can be justified as the only course of action. The structure of crystalline CoA_2 can probably be determined by X-ray diffraction¹³ so that we shall not include any special consideration of this. Of course, it may be hoped that the structure of the crystalline solid will have certain basic features in common with the structures in the other phases and thus indirectly provide information concerning the others.

We consider it plausible that the oligomers are built up of CoA_2 units in which the four oxygen atoms form a more or less square array about the cobalt atoms, though the entire CoA_2 units may deviate considerably from planarity, perhaps in the same manner as does the CoA_2 portion of $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$,¹⁵ or in some other way. Two of these units could then combine so that their mean CoO_4 planes lie approximately parallel but offset sufficiently to put one oxygen atom in each unit above or below the cobalt atom of the other unit. In such a dimer, there would, at all events, be a considerable acentric component to the ligand field about each cobalt atom. This dimer could add additional CoA_2 units on both sides to build up the higher oligomers, in which the cobalt atoms of the terminal units would still experience markedly acentric fields, although the cobalt atoms in nonterminal units would be more centrosymmetrically situated. This type of structure would be consistent with the indications that there may be some degree of special stability for the dimer and with the formation of trimers and still higher oligomers. The fact that the spectrum of crystalline CoA_2 is better resolved than those of CoA_2 oligomers in solution or of glassy CoA_2 probably reflects the existence of greater and longer-range ordering in the crystalline substance.

(14) It may be recalled⁵ that it takes temperatures of $\sim 200^\circ$ to produce even a few per cent of monomer from $(\text{NiA}_2)_3$.

(15) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

The emphasis on acentricity in the ligand field experienced by the cobalt atoms is in connection with the intensity of the visible absorption band observed in the oligomers. At the highest concentrations studied ϵ_{\max} is about 70 and this is necessarily a lower unit. On the other hand, for $\text{CoA}_2 \cdot 2\text{H}_2\text{O} - \text{CoA}_2 \cdot 2\text{CH}_3\text{OH}$, as shown in Fig. 4, the ϵ_{\max} values are only about 40% of this. Since it is known that acentricity can lead to enhancement of intensities by relaxing the Laporte selection rule, and since the structure of $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$ is quite similar in many respects to the sort of local environment of cobalt atoms in the structure we have suggested for the oligomers, we believe that in the oligomers there will be distortions not found in $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$, such as twisting or bending of the plane of the four close oxygen atoms, which introduces an acentric component into the ligand field about the non-terminal cobalt atoms.

The effective magnetic moment previously reported⁴ for CoA_2 (4.93 B.M. at 300°) is quite consistent with the roughly octahedral environment of the cobalt atoms in the proposed structure for the oligomers. This structure, it may be noted, is similar in its gross features to the one proposed by Holm for the oligomers of certain nickel(II) salicylaldimine complexes.¹⁶

A few additional comments and observations may now be recorded. The ultraviolet spectrum of CoA_2 has been examined at concentrations between 10^{-3} and 10^{-5} M in chloroform at $\sim 25^\circ$. No deviations from Beer's law were detected. This supports the conclusion that virtually complete dissociation of oligomers has occurred already at concentrations of 10^{-2} – 10^{-3} M, so that Beer's law should be obeyed at all lower concentrations.

The tetrahedral structure of CoA_2 answers the question of whether steric factors play any significant role in producing the tetrahedral structure of $\text{Co}(\text{DPM})_2$,

(16) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

in preference to a planar structure for this molecule. Using reasonable dimensions for the $\text{Co}(\text{DPM})_2$ molecule in a planar configuration, it appears that repulsion between *t*-butyl groups cannot be very great, so that if such repulsion is the critical factor, the relative stabilities of the two configurations must be little different. The results for CoA_2 , where no repulsive forces come into play in the monomer, show that the tetrahedral configuration is inherently the more stable at normal temperatures. At the same time, if our conjectures about the structures of the oligomers are correct, the energy of the tetrahedral configuration is not likely to be more than perhaps 20 kcal./mole below that of the planar one.

The results of another experiment permit us to estimate a lower limit for the enthalpy difference between planar and tetrahedral $\text{Co}(\text{DPM})_2$. Attempts were made to incorporate $\text{Co}(\text{DPM})_2$ in crystalline $\text{Ni}(\text{DPM})_2$ (in which the molecules are planar) by growing crystals of the latter from solutions containing comparable concentrations of $\text{Co}(\text{DPM})_2$ and $\text{Ni}(\text{DPM})_2$. No cobalt could be detected spectroscopically in the crystals obtained, and we estimate that the limit of detectability must be a Co/Ni ratio of about 10^{-2} . Using an elementary statistical mechanical treatment,¹⁷ it can easily be shown that for the process of replacing a mole fraction, X , of $\text{Ni}(\text{DPM})_2$ molecules by $\text{Co}(\text{DPM})_2$ molecules at 300°K., the quantity $T\Delta S$ is about 3.0 kcal./mole of $\text{Co}(\text{DPM})_2$ when $X \approx 10^{-2}$. Assuming that the enthalpy of substituting *planar* $\text{Co}(\text{DPM})_2$ for $\text{Ni}(\text{DPM})_2$ would be ~ 0 , the equilibrium condition, $\Delta F = 0$, for the actual process can be assumed to hold when the above $T\Delta S$ term equals $-\Delta H$ for the process of changing tetrahedral $\text{Co}(\text{DPM})_2$ to planar $\text{Co}(\text{DPM})_2$, giving 3.0 kcal./mole as a lower limit on this enthalpy.

(17) See G. S. Rushbrooke, "Introduction to Statistical Mechanics," Oxford University Press, 1949, Chapter 14, for a discussion of almost exactly the problem we have treated.

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Relative Enthalpies of Formation of Some Tetrachlorometallate Ions^{1a}

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The heats of solution of the series of compounds $[\text{As}(\text{C}_6\text{H}_5)_3\text{CH}_3]_2[\text{MCl}_4]$, $\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$, have been measured. Using these results, the problem of the relative stabilities of the $[\text{MX}_4]^{2-}$ species is discussed, with particular reference to the reaction $[\text{MCl}_4]^{2-}(\text{aq}) + \infty\text{H}_2\text{O} = [\text{M}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$. It is concluded that the differences in crystal field stabilization energies of the $[\text{MCl}_4]^{2-}$ and $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ions vary in about the same way as the enthalpies of the overall process and thus provide a fairly good first approximation to the relative enthalpies of these reactions. The role of other energy contributions is also discussed briefly.

Introduction

In order to determine the relative enthalpies of formation of $[\text{MCl}_4]^{2-}$ ions, in which the metal, M, is Mn, Fe, Co, Ni, Cu, and Zn, calorimetric measure-

ments have been carried out on the series of salts $[(\text{C}_6\text{H}_5)_3\text{CH}_3\text{As}]_2\text{MCl}_4$. All of these except the one containing copper have been shown by Pauling² to be iso-morphous, belonging to the space group P2₁3 (No. 198).

(1) (a) Research supported by the United States Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation.

(2) (a) P. Pauling, Ph.D. Thesis, University College, London, 1960; for partial reports see (b) N. S. Gill, R. S. Nyholm, and P. Pauling, *Nature*, **182**, 168 (1958); (c) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).