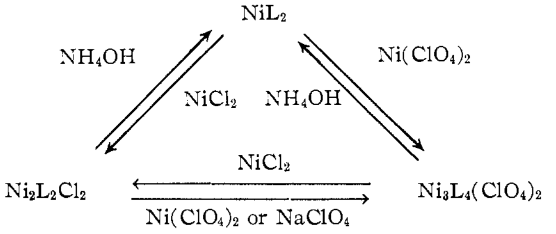
structure for the oxalato complex. A polymeric oxalato complex would indicate the symmetrical form for complexes of this type.

The three types of complexes which 2-(2-mercaptoethyl)-pyridine forms with divalent metal ions of the nickel group have all been observed with other ligands. However, no other ligand has been observed to form all three types. These results emphasize the importance of reaction conditions and type of anion on the structure of complexes and, also, show the versatility of the mercaptide donor in forming complexes of varying structure.

The different types of complexes are readily converted one to another under the proper conditions. Thus, with nickel as the metal, the reactions shown in Scheme I have been carried out. The products in these reactions (which are described in the Experimental section) were identified by infrared spectra and analysis.

SCHEME I



Complexes with Other Metals.—The attempted preparation of complexes of 2-(2-mercaptoethyl)-pyridine with metals other than those of the nickel group was unsuccessful, except in the case of cobalt. A product of stoichiometry $Co_3L_4Cl_2 \cdot 2HCl$ was obtained in the reaction of $CoCl_2$ with the ligand in methanol. The structure of this complex remains in question.

Mixed Metal Complexes.—In the investigations of Jicha and Busch[5,6] with complexes of β-mercaptoethylamine, a number of mixed metal derivatives containing complex ions of the type shown in structure V were prepared by reaction of bis complexes $M(NH_2CH_2CH_2S)_2$, with metal salts. In this investigation also, attempts were made to prepare bridged derivatives containing more than one metal by reaction of the complexes ML_2 with metal salts. The results of the reaction of PdL_2 with Ni^{+2} have already been mentioned. In this case the mixed metal complex $NiPd_2L_4(ClO_4)_2$ was obtained.

The reactions of NiL_2 with several divalent metal salts of the first transition series were also investigated. Metal ions used were Mn^{+2}, Fe^{+2}, Co^{+2}, and Cu^{+2}. The only mixed metal complex obtained was $CoNi_2L_4(ClO_4)_2$, which was prepared by shaking the solid NiL_2 with a methanolic solution of $Co(ClO_4)_2$. The other metal ions appear to catalyze oxidation of the ligand and attempted isolation of stoichiometric products was unsuccessful.

The preparation of the mixed metal Co–Ni and Ni–Pd complexes in the manner described is a strong indication that complexes of the type ML_2 are *cis* in configuration. A *trans* configuration would require dissociation of the ligand from the metal during the course of the reaction and should lead to nonstoichiometric ratios of metals in the resulting bridged complexes.

Acknowledgment.—The financial support of the U. S. Army Medical Research and Development Command is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Preparation and Reduction of Bis-(3-nitro-2,4-pentanediono)-beryllium

BY RICHARD M. KLEIN[1] AND JOHN C. BAILAR, JR.

Received February 21, 1963

Reaction of 2,4-pentanedione with beryllium nitrate trihydrate in acetic anhydride gave bis-(3-nitro-2,4-pentanediono)-beryllium (compound I). This was reduced catalytically to the corresponding amine (II). Bis-(2,4-pentanediono)-beryllium reacted in this nitrating medium to yield a polymeric nitrated complex containing hydroxo bridges (VI). This was converted to either the methoxo or ethoxo bridged complexes (VII and VIII) by boiling in methanol or ethanol. These were shown by molecular weight studies to be partially trimeric.

The nitration of chromium(III), cobalt(III), and rhodium(III) acetylacetonates has been reported by Collman and co-workers,[2] who used cupric nitrate trihydrate in acetic anhydride as the nitrating agent. Their attempts to reduce these to the corresponding amino-substituted complexes, however, were unsuccessful.[3]

The amino type of complex is of interest because of the reactions which the functional group might undergo, particularly diazotization, which could be followed by the substitution of various other functional groups onto the chelate ring.

---

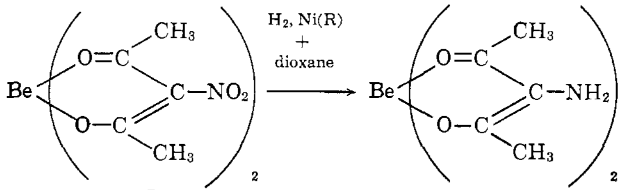
(1) Abstracted from a portion of the Ph. D. thesis of Richard M. Klein, 1963.

(2) J. P. Collman, R. L. Marshall, W. L. Young, III, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

(3) Since submission of this paper, it has been brought to our attention that more recent experiments have resulted in the reduction of the nitro-substituted chromium(III) acetylacetonate to the amino chelate. The latter substance forms a stable diazonium salt. J. P. Collman and M. Yomada, Southeastern Regional Meeting of the American Chemical Society, Gatlinberg, Tenn., Nov., 1962; *Chem. Ind.* (London), in press.

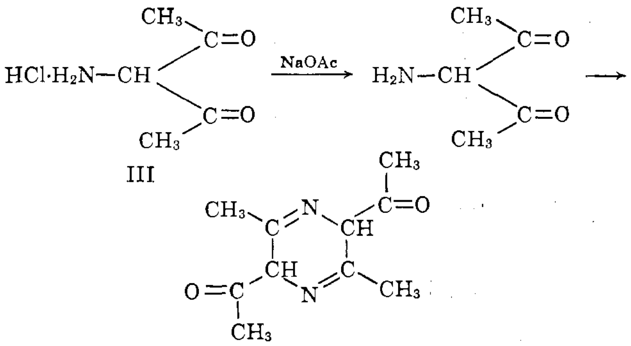
We have prepared bis-(3-nitro-2,4-pentanediono)-beryllium (compound I) and catalytically reduced it to the amino-substituted complex (II), reactions of which will be discussed in a future paper. The nitrated complex formed on reaction of acetylacetone with a solution of beryllium nitrate trihydrate in acetic anhydride and was obtained in a nearly quantitative yield when the reaction mixture was poured into water.

The reduction of I was carried out at 50 p.s.i., using 15% by weight of a Raney nickel catalyst, with carefully purified dioxane as the solvent. The theoretical amount of hydrogen was taken up, but decomposition also occurred and the yield of yellow solid product was quite low.



I II

An attempt was made to prepare compound II by adding an aqueous solution of 3-amino-2,4-pentanedione hydrochloride (III) to a beryllium nitrate solution containing an excess of a sodium acetate buffer. As soon as the ligand was neutralized by the sodium acetate, however, the solution darkened and, on standing, yellow needles formed in the reaction medium. These analyzed quite well for the cyclic diimine (IV) which would be formed by the intermolecular self-condensation of the free diketo amine. Since the same needles could also be obtained from the decomposed reduction solution after II had been isolated, it appears that II is quite labile in solution and that, as the ligand dissociates from the beryllium, it undergoes self-condensation. This would explain the low yield of the amine.

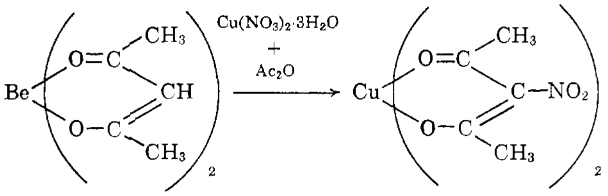


III

IV

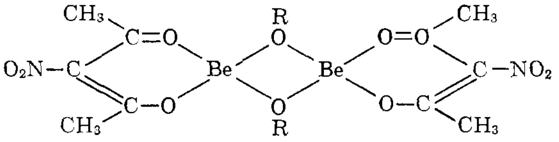
Infrared spectra in Nujol mulls confirm that the amino complex has been isolated. I has a strong peak at 1535 cm.$^{-1}$ which is assigned to the N–O stretching mode, and a peak at 1130 cm.$^{-1}$ attributed to the C–N absorption. II shows no absorption at 1535 cm.$^{-1}$, has the C–N peak shifted to 1205 cm.$^{-1}$, and also has a strong peak at 3410 cm.$^{-1}$, which represents the N–H stretching frequency.

The lability of these substituted beryllium acetylacetonate complexes was further illustrated when attempts were made to nitrate beryllium acetylacetonate directly. When this substance was dropped into a solution of cupric nitrate trihydrate in acetic anhydride and the resulting deep blue solution was poured into water, green needles of bis-(3-nitro-2,4-pentanediono)-copper(II) (compound V) were obtained. This is surprising, since copper acetylacetonate and its bromine-substituted derivative have both been shown to be far more labile (in chloroform solution) than the corresponding beryllium compounds.[4] Our result suggests, however, that the nitrated copper complex is far more stable than the beryllium compound in acetic anhydride. The result cannot be due to solubility effects, for the copper complex is much more soluble in this medium than is the beryllium compound.



V

When beryllium acetylacetonate was nitrated in the beryllium nitrate–acetic anhydride reagent, reaction with the excess beryllium occurred to produce the hydroxo bridged complex VI.



VI, R = H
VII, R = CH_3
VIII, R = CH_2CH_3

When VI was refluxed in methanol, it first dissolved, but a precipitate with the corresponding methoxo bridged structure (VII) formed about 30 sec. later. Dissolving either VI or VII in hot ethanol and then cooling produced the ethoxo bridged compound (VIII or IX). These results are unexpected, since complexes containing methoxo and ethoxo bridges are unusual.

These bridged complexes were characterized by elemental analyses, infrared data, and molecular weight measurements. The infrared spectrum for VI shows a sharp peak at 3590 cm.$^{-1}$ which is assigned to the O–H stretching mode. VII and VIII have no peaks in this region, but show bands at 1200 and 1175 cm.$^{-1}$, respectively, which are not present in VI, and which are attributed to the C–O bond in the bridge.

The high molecular weights of VII and VIII indicate that the complexes are partially trimeric, as exemplified in structure IX.

The dimeric and trimeric structures would be identical in elemental analyses and spectral properties. Hence, the only justification for the more highly polymeric

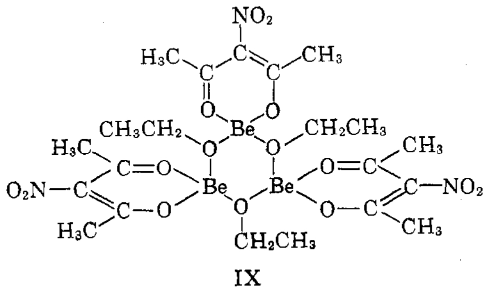
---

[4] R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

TABLE I

ANALYTICAL DATA FOR BRIDGED NITRATED COMPLEXES

Compound	Proposed bridge	Elemental analysis						Molecular wt.			Infrared O–X peak, cm.$^{-1}$
		C		H		N					
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd., dimer	Calcd., trimer	Found	
VI	OH	35.3	35.7	4.12	4.24	8.23	8.12			Insoluble	3590 s
VII	OCH_3	39.1	38.4	4.89	4.83	7.62	7.66	368	556	515	1200 m
VIII or IX	OC_2H_5	42.4	41.2	5.56	5.40	7.07	7.70	396	594	575	1175 s



IX

structures can be the high molecular weight values. Table I sums up the data for these compounds.

Attempts were also made to nitrate and complex dibenzoylmethane in the beryllium nitrate–acetic anhydride reagent, but these resulted only in the formation of bis-(dibenzoylmethano)-beryllium.

Experimental[5]

Bis-(3-nitro-2,4-pentanediono)-beryllium (Compound I).—Beryllium nitrate trihydrate (30 g., 0.152 mole) was dissolved in 30 ml. of acetic anhydride with cooling to prevent splattering caused by the highly exothermic reaction. 2,4-Pentanedione (30 g., 0.300 mole) was added dropwise with cooling and, when about half of this ligand had been added, a fine precipitate formed. After the addition was complete, the mixture was stirred for 1 hr. at room temperature and then poured into ice water. The light yellow precipitate was recrystallized from approximately 1 l. of absolute ethanol, giving yellow needles which melted at 186°; yield of unrecrystallized product 38.4 g. (86.4%).

Anal. Calcd. for $C_{10}H_{12}O_8N_2Be$: C, 40.2; H, 4.02; N, 9.36; mol. wt., 297. Found: C, 40.54; H, 4.25; N, 9.46; mol. wt., 290.

Preparation of Bis-(3-amino-2,4-pentanediono)-beryllium (II).—The dioxane used as a solvent for this preparation was purified by the method (a) described by Fieser,[6] and was stored over sodium wire. The bottle in which the reduction was carried out was alternately evacuated and flushed with nitrogen three times before the reactants were added. This step was critical, as no reduction took place if it was omitted. Into the reaction bottle were placed bis-(3-nitro-2,4-pentanediono)-beryllium (2 g., 0.0063 mole) and about 20 ml. of dioxane. Approximately 15% by weight of a Raney nickel catalyst was added, and the mixture was treated with hydrogen on a shaker apparatus at 50 p.s.i. for 1 hr. The hydrogen pressure fell approximately 3.2 p.s.i. (theoretical, 3.16 p.s.i.) and the solution turned from yellow to dark red. The catalyst was filtered, and the volume of the solution was reduced on a rotary evaporator until a large amount of a fine precipitate formed. This was filtered and washed quickly with acetone, giving a light yellow powder which melted with decomposition at 248°; yield 0.20 g. (12.5%).

Anal. Calcd. for $C_{10}H_{16}N_2O_4Be$: C, 50.7; H, 6.75; N, 11.8; Be, 3.79. Found: C, 50.69; H, 6.90; N, 11.4; Be, 4.00.

Attempted Reaction of 3-Amino-2,4-pentanedione Hydrochloride with Beryllium Nitrate Trihydrate.—3-Amino-2,4-pentanedione hydrochloride[7] was prepared by the catalytic reduction of the corresponding oxime, which had been synthesized according to the directions of Wolff, *et al.*[8] The reduction of the oxime (20 g., 0.154 mole) was carried out in 155 ml. of an ethanol solution containing a slight excess of aqueous hydrochloric acid. A Pd–C A-100 catalyst[9] was used, and the amine hydrochloride was obtained as a white solid by pouring the reaction mixture into absolute ether. The product was identified by its melting point of 161°. Upon addition of an aqueous solution of the amine hydrochloride to a solution of beryllium nitrate trihydrate which contained an excess of sodium acetate, the solution turned dark immediately. The yellow needles which separated on standing were purified by sublimation under vacuum and melted at 100°. These analyzed well for the diimine IV.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.8; H, 7.22; N, 14.40; Be, 0. Found: C, 62.6; H, 6.73; N, 14.61; Be, 0.

Reaction of Bis-(2,4-pentanediono)-beryllium with Copper(II) Nitrate Trihydrate in Acetic Anhydride (V).—Copper(II) nitrate trihydrate (15.15 g., 0.0627 mole) was dissolved in 30 g. of acetic anhydride and 15 g. of glacial acetic acid with cooling in order to keep the temperature at 35°. To this was added dropwise, with stirring and cooling, a solution of bis-(2,4-pentanediono)-beryllium (10 g., 0.0507 mole) in 12 g. of acetic anhydride and 8 g. of glacial acetic acid. The dark blue solution was stirred for 15 min. after the addition was complete and then poured into ice water, giving 7.1 g. of a green powder (40.2%). Green needles were obtained on recrystallization from benzene. These melted with decomposition at 235°.

Anal. Calcd. for $C_{10}H_{12}O_8N_2Cu$: C, 34.19; H, 3.42 N, 7.97. Found: C, 34.36; H, 3.59; N, 7.94.

Bis-(2,4-pentanediono)-μ-diol-diberyllium (VI).—Beryllium nitrate trihydrate (12.35 g., 0.0627 mole) was dissolved in 30 g. of acetic anhydride and 15 g. of glacial acetic acid with cooling. Bis-(2,4-pentanediono)-beryllium (10.0 g., 0.10 mole) was added dropwise to this solution, and after about four-fifths of the complex had been added, a light yellow precipitate began to form. On completion of the reaction, the mixture was poured into ice water and the solid was collected. The yellow powder melted with decomposition at 246°.

Anal. Calcd. for $C_{10}H_{14}N_2O_{10}Be_2$: C, 35.3; H, 4.12; N, 8.23. Found: C, 35.71; H, 4.24; N, 8.12.

Preparation of Polymeric Bis-(2,4-pentanediono)-μ-dimethoxodiberyllium (VII).—Part of the product from the preceding preparation was boiled in absolute methanol. Approximately 30 sec. after complete solution was effected, a large amount of a yellow precipitate formed, m.p. 220°.

Anal. Calcd. for $C_{12}H_{18}N_2O_{10}Be_2$ or $C_{18}H_{27}N_3O_{15}Be_3$: C, 39.1; H, 4.89; N, 7.62; mol. wt. dimer, 368; trimer, 552. Found: C, 38.44; H, 4.83; N, 7.66; mol. wt., 515.

Preparation of Tris-(2,4-pentanediono)-μ,μ',μ''-triethoxotriberyllium (IX).—Either VI or VII was boiled in just enough absolute ethanol to completely dissolve the compound. On cooling the solution, a yellow solid was obtained, m.p. 203°.

Anal. Calcd. for $C_{14}H_{22}N_2O_{10}Be_2$ or $C_{21}H_{33}N_3O_{15}Be_3$: C, 42.4; H, 5.56; N, 7.07; mol. wt. trimer, 594. Found: C, 41.21; H, 5.48; N, 7.70; mol. wt., 575.

---

[5] Molecular weight data were taken in benzene solution by vapor pressure lowering. Infrared spectra were determined in Nujol mulls on a Perkin–Elmer Model 21 infrared spectrophotometer.

[6] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 285.

[7] K. L. Hoy and W. H. Hartung, *J. Org. Chem.*, **23**, 967 (1958).

[8] V. L. Wolff, P. Bock, G. Lorentz, and P. Trappe, *Ann.*, **325**, 134 (1902).

[9] W. Cash, F. Semeniuk, and W. Hartung, *J. Org. Chem.*, **21**, 999 (1956).

Acknowledgment.—We are grateful to Mr. J. Nemeth and his staff for the elemental analyses and molecular weight data and to the National Science Foundation and United States Air Force (the latter through Contract 7918) for their financial support of this work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Reactions of Coordination Compounds. Polymers from 3-Substituted Bis-(β-diketone)-beryllium Complexes

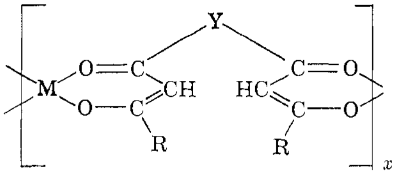
BY RICHARD M. KLEIN[1] AND JOHN C. BAILAR, JR.

Received February 21, 1963

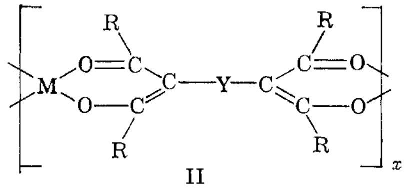
The preparations of bis-(ethyl benzoylacetoacetato)-beryllium, bis-(diacetylcarbinol)-beryllium, and bis-(3-aminoacetylacetonato)-beryllium (compounds III–V) are described. These complexes react through their functional groups with appropriate difunctional organic molecules in a melt or in solution to produce metal-containing polyesters, polyamides, polyurethanes, polysiloxanes, and polysilazanes. The polymers are quite unstable at temperatures above 200°, and the relative heat stabilities are well accounted for by the inductive and resonance effects produced by the various substituent groups.

Several investigations have been made into the preparations of polymeric bis-(β-diketone) complexes.[2]

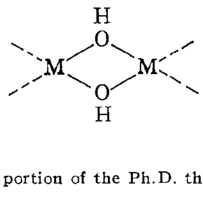
The syntheses were all carried out by allowing a bis-(β-diketone) to react with various metal ions under melt, solution, or interfacial polymerization conditions. It was hoped that polymers with structure I or II would thus be formed. Here, Y can be any linking group, such as an alkyl, aryl, or sulfonic group, and R represents an alkyl, aryl, or substituted alkyl substituent. Oh[2] observed, however, the formation of polymers containing diol bridges as well as those in which the metal ions were bound together solely through the diketone ligands.



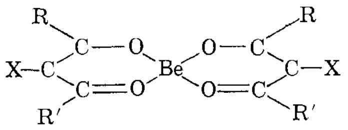
I



II

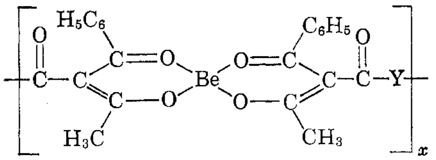


We have used a different method to prepare a series of beryllium β-diketone polymers. Complexes with chemically active functional groups substituted on the number 3 carbon atom of acetylacetone or benzoylacetone were allowed to react with various difunctional organic molecules. Specifically, the monomeric beryllium complexes which were prepared were those of ethyl benzoylacetoacetate (III), diacetylcarbinol (IV), and 3-aminoacetylacetone (V).

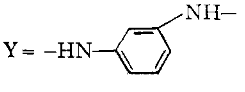


III, $X = OOCC_2H_5$; $R = CH_3$; $R' = C_6H_5$
IV, $X = OH$; $R = R' = CH_3$
V, $X = NH_2$; $R = R' = CH_3$

Polyesters and polyamides were formed from III in melt systems and IV and V were allowed to react with diphenyldichlorosilane, terephthaloyl chloride, and diisocyanates in order to obtain polymeric compounds. The polymers which were prepared are shown in formulas VI–XVI.



VI, $Y = -OCH_2CH_2O-$
VII, $Y = -HN(CH_2)_6NH-$
VIII, Y =



---

[1] Abstracted from a portion of the Ph.D. thesis of Richard M. Klein, 1963.

[2] For example, J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711 (Nov. 17, 1953); W. C. Fernelius and co-workers, "Coordination Polymers," W.A.D.C. Technical Report 56-203, Parts I, II, and III, Wright Air Development Center, Dayton, Ohio, 1958; J. S. Oh, Thesis, Doctor of Philosophy, University of Illinois, 1961; R. W. Kluiber and J. W. Lewis, *J. Am. Chem. Soc.*, **82**, 5777 (1960); W. C. Drinkard, D. Ross, and J. Wiesner, *J. Org. Chem.*, **26**, 619 (1961).