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

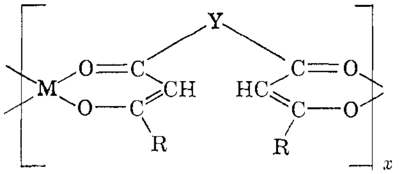
BY RICHARD M. KLEIN[1] AND JOHN C. BAILAR, JR.

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.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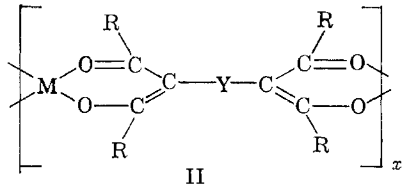
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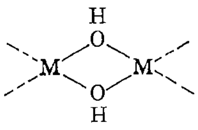
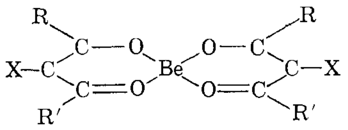
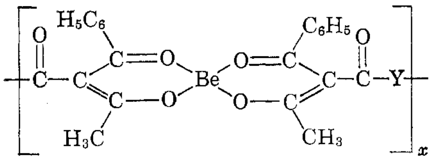


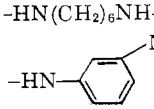
We have used a different method to prepare a series of beryllium β-diketone polymers. Complexes with chemically active functional groups substituted on the number 3 carbon atom of acetylacetone or benzoylacetone were allowed to react with various difunctional organic molecules. Specifically, the monomeric 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, $Y =$ 

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

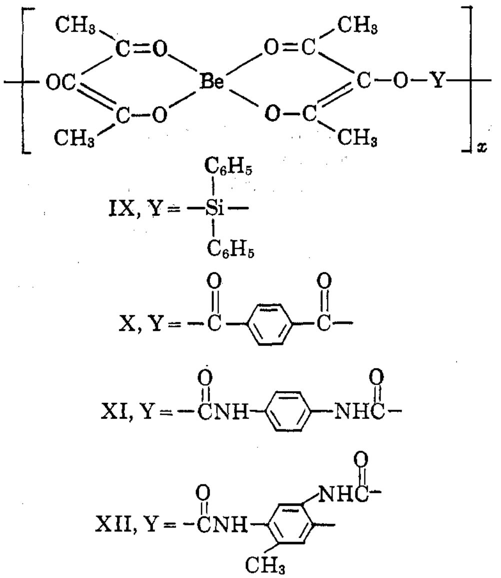
[2] For example, J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711 (Nov. 17, 1953); W. C. Fernelius and co-workers, "Coordination Polymers," W.A.D.C. Technical Report 56-203, Parts I, II, and III, Wright Air Development Center, Dayton, Ohio, 1958; J. S. Oh, Thesis, Doctor of Philosophy, University 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).

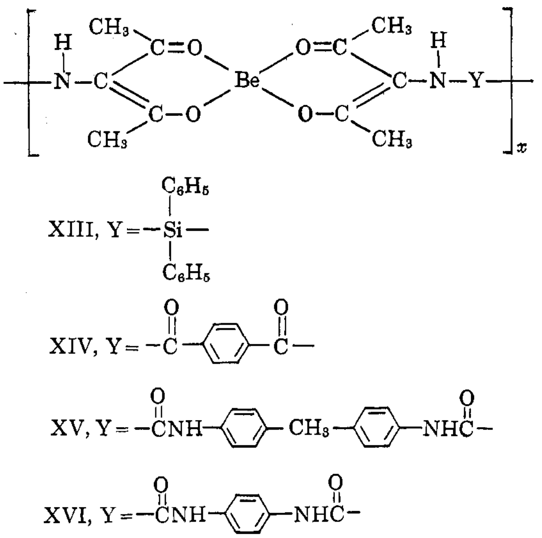
TABLE I

PHYSICAL PROPERTIES OF POLYMERS FROM SUBSTITUTED BERYLLIUM–BIS-(β-DIKETONE) COMPLEXES

Polymer	Method of prepn.	Description	Melting or softening point, °C.	Solubility in nonpolar solvents[a]
VI	Melt	Hard yellow glass	118	Sol.
VII	Melt	Red tacky glass	Room temp.	Sol.
VIII	Melt	Hard yellow glass	65	Sol.
IX	Melt	Solid brittle brown glass	60	Sol.
X	Melt	Brittle brown glass	260	Sl. sol.
XI	Solution	Tough white cake	250 dec.	Insol.
XII	Solution	Tough white cake	250 dec.	Insol.
XIII	Solution	Tan powder	200 dec.	Insol.
XIV	Solution	White powder	>330	Insol.
XV	Solution	Tough white cake	280 dec.	Insol.
XVI	Solution	Tough white cake	290 dec.	Insol.

[a] *e.g.*, benzene, toluene, carbon tetrachloride, chloroform.





Experimental

Ethyl benzoylacetoacetate[3] and diacetylcarbinol[4] were prepared according to directions given in the literature.

Preparation of Complexes. Bis-(3-aminoacetylacetonato)-beryllium (V).—The synthesis and properties of this compound have been reported in a previous paper.[5] This melts with decomposition at 248°.

Bis-(ethyl benzoylacetoacetato)-beryllium (III).—Ethyl benzoylacetoacetate (10.0 g., 0.427 mole) was added with rapid stirring to beryllium nitrate trihydrate (4.2 g., 0.0213 mole), which was dissolved in a mixture of 32 ml. of water saturated with sodium acetate and 50 ml. of ethanol. A precipitate formed almost immediately, and after 2 hr. the mixture was cooled in an ice bath. The white solid, which was collected by suction filtration, was recrystallized twice from absolute ethanol, yielding 5.5 g. (54.2%) of white crystals, melting at 125–126°.

Anal. Calcd. for $C_{26}H_{26}O_8Be$: C, 65.7; H, 5.36. Found: C, 65.69; H, 5.57.

Bis-(diacetylcarbinol)-beryllium (IV).—To a rapidly stirred solution of 11 g. of beryllium nitrate trihydrate (0.0557 mole) in 75 ml. of a saturated aqueous solution of sodium acetate, was added 12.5 g. of diacetylcarbinol (0.108 mole). This mixture was stirred overnight, cooled in an ice bath, and the solid which formed was collected by suction filtration. It was washed well with ice water and recrystallized from absolute methanol, yielding 2.0 g. of creamy white needles (15.5%). The product darkened at 240° but was still solid at 340°.

Anal. Calcd. for $C_{10}H_{14}O_6Be$: C, 50.25; H, 5.87; Be, 3.77. Found: C, 50.53; H, 5.98; Be, 3.43.

Preparation of Polymeric Compounds.—The analytical data and the physical properties of the polymers are given in Tables I and II.

Melt Polymerization Reactions (Compounds VI–X).—These were carried out in an oven-dried 24-ml. distilling flask. In the case of the polymers from compound III, the side arm led to a condenser, and the whole system was alternately evacuated and flushed with nitrogen three times. When the melt polymers from compound IV were being prepared, the side arm led into a flask containing a pyridine–ether solution.

Equimolar amounts of reagents were used in all preparations except that of polymer VI, in which case there was a 2.5:1 molar ratio of ethylene glycol to complex. The ethylene glycol was purified by boiling it with sodium for 1 hr. and then distilling from sodium. The *m*-phenylenediamine used in preparing compound VIII was freshly purified by recrystallization from benzene. Hexamethylenediamine was the co-monomer used for the preparation of polymer VII.

The polymerizations were carried out by heating the molten mixture at 175° and atmospheric pressure for a period of from 2 to 6 hr. while purified nitrogen was passed over it and then heating for an additional 1 to 2 hr. at 200° and a pressure of 1 mm. (compound X was heated at 135° for 2 hr. and then at 200° and 1 mm. for 30 min.). Ethanol distilled during the preparations of compounds VI, VII, and VIII, and white fumes of hydrogen chloride appeared when compound IV was allowed to react with diphenyldichlorosilane or terephthaloyl chloride to form

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[3] R. L. Shriner, A. G. Schmidt, and L. J. Roll, *Org. Syn.*, **18**, 33 (1938).

[4] H. Böhme and H. Schneider, *Ber.*, **91**, 1100 (1958).

[5] R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1187 (1963).

TABLE II

ANALYTICAL DATA FOR POLYMERS FROM SUBSTITUTED BERYLLIUM–BIS-(β-DIKETONE) COMPLEXES

		Analysis[a]								
		C		H		N		Be		
Polymer	Yield, %	Calcd.[b]	Found	Calcd.[b]	Found	Calcd.[b]	Found	Calcd.[b]	Found	Mol. wt.[c]
VI	82.5	64.75	64.23	4.50	4.74			2.02	2.31	1013
VII	92.3	67.3	66.12	6.02	7.14	5.62	5.53	1.81	1.49	574
VIII	>100[e]	68.4	68.20	4.48	5.61	5.69	4.38	1.83	1.49	624
IX	73.3	63.1	61.91	5.25	5.04			8.83[d]	9.64	997
X	85.6	58.5	57.33	4.34	4.29			2.44	3.5	
XI	93.9[f]	54.15	52.68	4.52	5.12	7.03	6.98	2.25	2.71	
XII	37.9[g]	55.25	52.85	4.84	5.35	6.78	6.74	2.18	2.16	
XIII	56.3	61.3	57.45	5.15	5.57	6.72	7.35	8.88[d]	9.80	
XIV	79.4[f]	58.9	54.15	4.90	5.42	7.63	6.20	2.45	3.38	
XV	78.7[g]	61.7	58.79	5.34	6.08	11.5	10.85	1.85	2.47	
XVI	88.9[f]	54.4	52.57	5.04	5.33	14.10	13.75	2.27	2.11	

[a] All solid compounds were dried in a drying pistol at 1 mm. and 78° for at least 12 hr. [b] Calculated for an infinite chain. [c] Measured in benzene by vapor pressure lowering. [d] Calculated for Be + Si. [e] Includes weight of some ethanol which remained in the side arm of the distilling flask. [f] Before extraction with methanol. [g] After extraction with methanol.

polymers IX and X. The hydrogen chloride reacted in the pyridine–ether mixture to give a white precipitate of pyridinium hydrochloride.

Preparation of Polyurethanes and Polyureas by Reactions of IV and V with Diisocyanates (Compounds XI, XII, XV, and XVI).—The dimethylformamide (DMF) used in these experiments was dried by shaking reagent grade DMF over potassium hydroxide pellets, then over powdered calcium oxide, and finally distilling from calcium oxide in a completely anhydrous system. The solvent was stored over a molecular sieve. The polymerization apparatus consisted of a 25-ml. flask fitted with a reflux condenser and protected from moisture by means of a silica gel drying tube. All glassware was dried overnight at 110°.

Equimolecular amounts of the monomeric complex and the appropriate diisocyanate (*p*-phenylenediisocyanate for XI and XVI, 2,4-toluenediisocyanate for XII, and 4,4′-diphenylmethanediisocyanate for XV) were dissolved in 10–20 ml. of DMF and heated with stirring at 110° for 2 hr. The yellow, viscous solution was then poured into water, producing a heavy white solid which was chopped to a fine powder in a Waring blender, washed with water, and extracted for 12–24 hr. with methanol.

Solution Polymerizations of Complex VI.—These were carried out in xylene which had been freshly distilled from sodium. All glassware had been dried in an oven at 110° and was protected from moisture by means of silica gel drying tubes. The apparatus consisted of a three-neck flask which was fitted with a reflux condenser and a nitrogen inlet tube.

Compound XIII.—Bis-(3-aminoacetylacetonato)-beryllium (0.202 g., 0.000852 mole) in 10 ml. of xylene was heated at reflux with stirring until solution was complete. When diphenyldichlorosilane (0.216 g., 0.000854 mole) was added to the hot solution, a light colored precipitate formed immediately, and white fumes rose in the condenser. The mixture was heated at reflux for 8 hr. while nitrogen was bubbled through it, and then filtered by suction, giving 0.1981 g. of a tan powder (56.3%). Evaporation of the yellow filtrate left an orange gum in the flask. This was discarded. The tan product was washed with benzene, in which it swelled up and darkened, but it turned light again on drying.

Compound XIV.—Bis-(3-aminoacetylacetonato)-beryllium (0.2120 g., 0.000894 mole) was refluxed in 10 ml. of xylene with stirring until complete solution was effected. Terephthaloyl chloride (0.1815 g., 0.000894 mole) was added to this hot solution, along with triethylamine (0.163 g., 0.00161 mole). A solid precipitated immediately and white fumes rose in the reflux condenser. The mixture was refluxed for 6 hr. while a stream of nitrogen was bubbled through it, after which the solvent was evaporated on a steam bath under reduced pressure. The tan solid was removed from the flask and washed well with water; yield 0.2063 g. (79.4%). The wash solution gave a positive test for chloride ion. The hygroscopic product was purified by extraction with methanol.

Infrared Spectra.—Spectra in the range of 600–4000 cm.$^{-1}$ were measured in a Nujol mull on a Perkin-Elmer Model 21 infrared spectrophotometer. Spectra in the range of 550–450 cm.$^{-1}$ were measured in a Nujol mull on a Beckman IR-5A infrared spectrophotometer using cesium bromide plates.

Thermal stability measurements were performed in a nitrogen atmosphere on a thermogravimetric balance similar to that described by Winslow and Matreyek.[6] The compounds were first heated to 140° for 12 hr. and any weight loss at this temperature, unless it was a substantial amount, was assumed to be due to evaporation of moisture. Heat stability is reported as the per cent weight loss at the designated temperature after a 12-hr. heating period at that temperature. Temperatures were constant to within ±5°.

Discussion

The analytical data and physical properties of the polymers are given in Tables I and II. The hydroxo and amino substituted complexes (IV and V) remained solid until decomposition took place (between 240 and 250°). The failure to melt before decomposing is thought to be due to intermolecular hydrogen bonding between the substituent groups which holds the structures in their solid phases until the decomposition temperatures of the complexes are reached.

Compound IV underwent melt polymerization with diphenyldichlorosilane and terephthaloyl chloride. This monomeric complex must then be reactive enough to dissolve in the liquid dichlorides as the reaction proceeds.

The polymers are generally similar in physical appearance to analogous, but purely organic, compounds. Thus, some of the polyesters, polyamides, and polysiloxanes are glasses at room temperature and can be drawn into fibers from the melt or from concentrated solutions. The polyurethanes and polyureas are tough, spongy, white solids. Those polymers which are soluble in benzene show low molecular weight values, however. This is thought to account for the low softening points of these polymers, and the compounds which are insoluble and melt at temperatures above 200° are likely to be of higher molecular weight.

Where wide discrepancies exist between the calculated and found analytical values for VII and VIII, it

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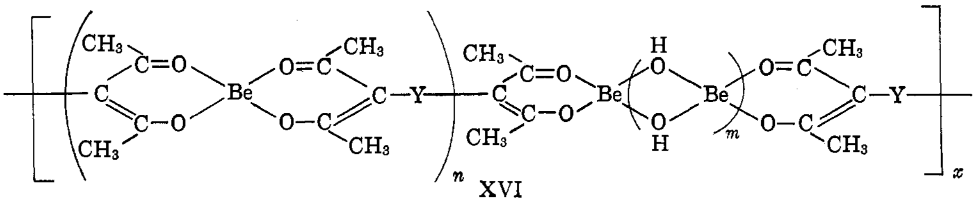
(6) F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

is thought that some benzene–acetone solvent has been retained by the polymer. This solvent mixture had to be used in order to remove these hard glasses from the reaction flask.

The slight discrepancies in the analytical values, and the unusual physical properties of the polymers which were prepared in solution, can be explained by a different theory. It is thought that the dissolved complexes become somewhat labile on heating and, while the reactions with the difunctional organic compounds take place, some of the ligand–beryllium bonds are broken. The beryllium ions can then be joined together by hydroxo bridge bonds to form the more highly polymeric structure XVI.


XVI

The ionic character imparted to this structure by the hydroxo bridges would cause the low solubility in nonpolar solvents and the infusibility which are characteristic of the polymers which were prepared in solution.

The infrared spectra of these compounds show some very weak, broad absorption bands in the 3400–3700 cm.$^{-1}$ region, but because of the number of such peaks, there are none which can definitely be attributed to O–H bridge bonds. Infrared analyses do indicate that a reaction has taken place between the co-monomers in every polymerization experiment. Thus, new carbonyl peaks appear when a polyester, polyamide, polyurethane, or polyurea is formed, and phenyl–silicon bonds are evident in the siloxane and silazane derivatives. Disappearance of the peaks which were due to the functional groups originally on the complexes is also noted.

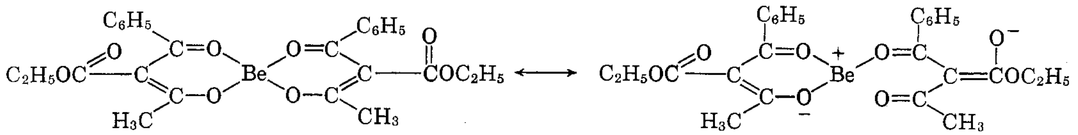
Thermal Stability Studies.—The thermal stability data for the polymers, and the monomeric complexes from which they were prepared, are given in Table III. These indicate, first of all, that the monomeric complexes are quite unstable toward heat. It is proposed that this instability is due to the weakening of the beryllium–oxygen bonds in the complexes by a combination of the inductive and resonance effects produced by the substituents on the chelate ring. The carboxyethyl, hydroxo, and amino groups all have negative inductive effects and thus withdraw electrons from the system, destabilizing the coordinate bonds. Furthermore, the resonance forms XVII–XIX can be drawn for the three complexes. It is seen that the beryllium–oxygen bonds are broken in all three of these structures. These structural features, which add to the tendency of the ligand to dissociate from the beryllium, result in a lowering of the decomposition temperature.

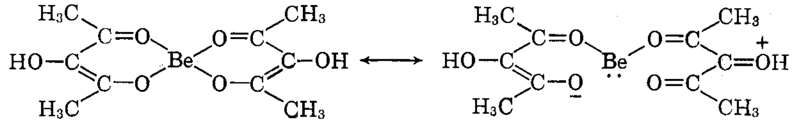
TABLE III

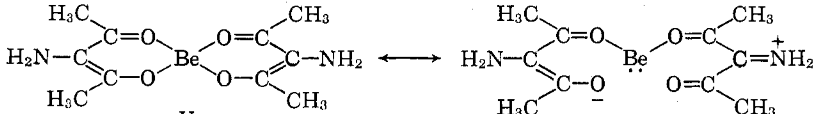
THERMAL STABILITY DATA

Compound	% decomposed after successive 12-hr. periods at designated temp. 140°	200°	250°	300°
III	...	3.97	44.5	56.7
VI	...	17.3	43.5	
VIII	...	14.1	27.1	39.2
IV	18.7	39.0	54.4	
IX	19.45	25.5	35.5	50.6
X	...	14.8	31.3	46.3
XI	...	23.8	39.7	
XII	...	19.6	32.1	53.5
V	...	27.4	40.3	57.8
XIII	...	29.4	46.1	61.7
XIX	...	1.66	20.3	44.5
XX	...	9.43	24.8	52.7
XXI	...	8.12	28.7	52.1

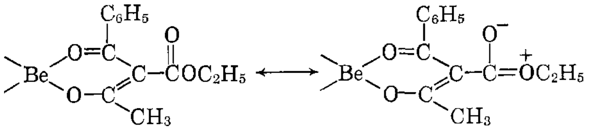
The explanation for the fact that complex III is far more stable than IV or V at 200° lies in the ability of III to assume an additional resonance form (XX).


III XVII


IV XVIII

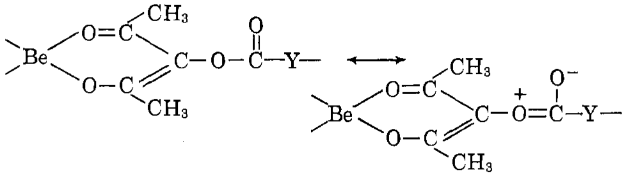

V XIX

This does not affect the beryllium–oxygen bond, but it does reduce the importance of resonance form XVII to the total structure and thus stabilizes the complex.

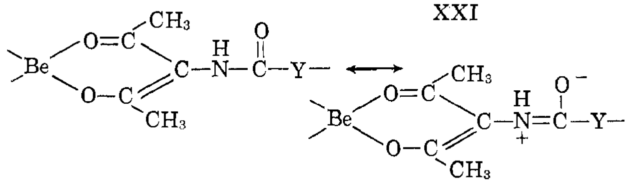


III XX

An interesting correlation is observed between the stability of the acetylacetonate complexes and the infrared absorption frequency for the metal–oxygen bond. The peak which occurs in the stable beryllium acetylacetonate complex at 500 cm.$^{-1}$ has been assigned by Martell to a nearly pure beryllium–oxygen stretching vibration.[7] A less stable acetylacetonate complex would be expected to show a decrease in the frequency of this absorption, due to the weakening of the beryllium–oxygen bond. Infrared spectra of the monomeric complexes prepared in this study show a definite shift toward lower frequencies for the metal–oxygen bond. Thus, the hydroxo, amino, and carboxyethyl substituted complexes have this peak occurring at 480, 477, and 473 cm.$^{-1}$, respectively. (Beryllium acetylacetonate shows a peak at 497 cm.$^{-1}$ on the same instrument.) The data for polymers IX–XVI in Table III show that these compounds generally are more stable than the monomeric complexes from which they are formed. This is due to the existence of the new resonance structures XXI and XXII for these polymers which cannot be written for the simple complexes.



XXI



XXII

Here, as in structure XX, the resonance form does not promote the breaking of the beryllium–oxygen bond, but decreases the importance of the resonance forms which do favor this dissociation. It is of interest to note that resonance forms like XXI and XXII cannot be written for the silicon-containing polymers, and these show no increased stability over the parent complex.

Polymers of type VI also offer no resonance possibilities which differ from those in the parent complex, and since these polymers now contain a linking chain, they are actually less stable than the monomeric complex itself.

The greatly increased stability which polymers of types XIV, XV, and XVI show at 200° is most likely due to the partial ionic character imparted to them by the formation of hydroxo bridges, as proposed in structure XVI.

Acknowledgments.—We wish to thank Mr. J. Nemeth and his staff for the analytical data which they measured and the National Science Foundation and United States Air Force (the latter through contract 7918) for their financial assistance.

[7] K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh 13, Pennsylvania

Circular Dichroism of Coordination Compounds. I. Splitting Patterns for Potassium Ethylenediaminetetraacetatocobaltate(III) and Model Compounds[1]

By BODIE E. DOUGLAS, ROLAND A. HAINES, and JOHN G. BRUSHMILLER

Received July 8, 1963

The optical absorption, optical rotatory dispersion (ORD), and circular dichroism (CD) data for the visible and near-ultraviolet regions have been compared for $K[Co(EDTA)]$, $Na[Co(en)(C_2O_4)_2]$, and $K[Co(en)(mal)_2]$. The two absorption bands for each compound are symmetrical, but the ORD curves reveal two components in the long wave length band and the CD curves reveal three components for each band. The signs of the CD peaks follow the same pattern for all three compounds only in the short wave length band. The $(-)_{546}$-$K[Co(en)(mal)_2]$ complex is assigned the Λ (or D) absolute configuration based on the CD data, ORD curves, and solubility data.

The spectrum of $K[Co(EDTA)]$ (EDTA = ethylenediaminetetraacetate ion) has been interpreted as indicating an essentially cubic crystal field[2] about Co(III) since the two bands in the visible region appear to be symmetrical on a wave length scale. The $[Co(en)(C_2O_4)_2]^-$ and $[Co(en)(mal)_2]^-$ (mal = malonate ion)

[1] This work was supported by a grant (AM02219-05S1) from the Division of General Medical Studies, Public Health Service. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 643 (1956).