

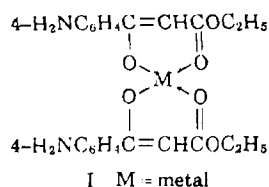
ORGANIC CHEMISTRY
 PHYSICAL PROPERTIES
 EVALUATION OF COMPOUNDS
 AND MATERIALS

Metal Chelates of Ethyl 4-Aminobenzoylacetate

I. GUY DONARUMA

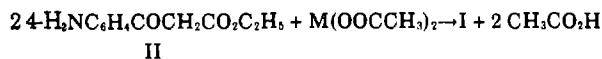
Clarkson College of Technology, Potsdam, N. Y.

WHILE ATTEMPTING TO PREPARE diamines of the type I, in order to use such diamines as comonomers in polymerization studies, it was found that using most of the common procedures for the preparation of chelates similar to I led only to the recovery of the ligand.



Therefore, a very convenient new technique was devised which allows the preparation of very pure chelates in 20 to 60 minutes.

It is known that toluene forms a binary azeotrope with either acetic acid or water (4) and that the composition of the toluene-acetic acid azeotrope is 66% toluene and 34% acetic acid at 105° and that the composition of the toluene-water azeotrope is 80.4% toluene and 19.6% water at 84.1°. These substances do not form a ternary azeotrope (1). Since metal acetates are readily available, it was decided to attempt to exchange acetic acid for ligand and thus form the desired chelate complex using toluene as a vehicle for removal of the acetic acid formed to drive the reaction to completion.



To test the idea, a number of well known ligands were put through the reaction with a variety of metal acetates. The results of these reactions are shown in Table I.

The data in Table I show that the reaction goes quite well. The yields of recrystallized product were good in all cases except where thorium acetate was used. It appears that in this case, the thorium acetate used was impure. Where the metal acetate employed was hydrated, the water azeotrope distilled off before the acetic acid azeotrope.

The reaction procedure was now applied directly to the synthesis of the desired complexes (I). Prior to working out the reaction conditions, 4-aminobenzoylacetate ethyl ester (II) (2) was synthesized by catalytic reduction of 4-nitrobenzoylacetate ethyl ester (III) (3). To our knowledge, no isolated complexes of II and III are known. Using the technique described above, the Pb(II), Zn(II), and Co(II) chelates of II were prepared, and the Fe(III) and Cu(II) complexes of III were prepared. Table II displays the results of these experiments.

In all reactions carried out, it was found desirable to use a slight excess of ligand. Where the products were insoluble in all available solvents, it was found desirable to employ 0.1 molar excess of ligand.

EXPERIMENTAL

It was not found necessary to use dry toluene to run the reactions because any water present in the toluene as well as water of hydration present in the metal acetate distilled off first.

Table I. Reaction of Several Ligands with Various Metal Acetates in Boiling Toluene

Ligand	Metal acetate	% Yield of Chelate
Acetylacetone	ThAc ^a	22 ^b
Oxine	CuAc ₂ ·H ₂ O	95 ^b
Acetylacetone	AlAc ₃	70 ^b
Acetylacetone	Al ₂ (SO ₄) ₃ ^c	65 ^b
Dibenzoylmethane	CuAc ₂ ·H ₂ O	68 ^b
Tropolone	CuAc ₂ ·H ₂ O	57 ^b

^aAc = CH₃CO₂⁻. ^bInfrared spectrum identical to that of an authentic sample. ^cThe acetate was not used here. The metal was precipitated with ammonia and the precipitate centrifuged, washed, and dissolved in acetic acid. The acetic acid solution was used in place of the metal acetate.

Table II. Preparation and Properties of Various Metal Complexes of Ligands II and III

Ligand	Metal Acetate	% Yield of Chelate	Metal Analyses		Infrared Data in cm. ⁻¹ ^a
			Calcd.	Found	
II	PbAc ₂ ·3H ₂ O	100 ^b	33.4	33.1	3450m, 3350m, 3235w, 3100w, 2975w, 2920w, 1726w, 1695w, 1680m, 1585s, 1520s, 1410s, 1325m, 1260w, 1255w, 1250w, 1215m, 1170s, 1155w, 1145w, 1000m, 925m, 820m
II	ZnAc ₂ ·2H ₂ O	100 ^b	13.6	13.2	3440m, 3350m, 3200w, 3160w, 2960w, 2900w, 1745w, 1675m, 1590s, 1525s, 1490w, 1450w, 1180s, 1040w, 1035w, 1000w, 955w, 910w, 845w, 835w
II	CoAc ₂ ·4H ₂ O	100 ^b	12.5	12.8	3350m, 3200w, 3100w, 2900w, 1725m, 1675m, 1610w, 1590s, 1525s, 1435m, 1420m, 1410s, 1395s, 1350w, 1325s, 1215m, 1175s, 1160s, 1035m, 1020m, 1000w, 975w, 955w, 945w, 925w, 915w, 885w, 840w, 820m, 815m
III	CuAc ₂ ·H ₂ O	41 ^{b,c}	11.9	11.6	2900w, 1610m, 1560s, 1535s, 1485m, 1360w, 1340s, 1315m, 1290s, 1215s, 1180m, 1110m, 1040s, 1015m, 920m, 865m, 845m
III	FeCl ₃ ^d	22 ^e	7.29	7.55	2920w, 1615w, 1580s, 1520s, 1485s, 1345s, 1320w, 1280s, 1205s, 1115m, 1030m, 1010w, 955w, 915w, 855w

^aw = weak absorption, m = medium absorption, s = strong absorption. ^bProduct was insoluble in all common solvents and did not melt up to 300°, but appeared to begin to decompose above 200°.

^cRecrystallized from chloroform in a Xohxlet extractor. ^dSame procedure employed as described in foot note c of Table I. ^eRecrystallized from chloroform and ligroin.

The quantity of toluene employed did not seem to be important as long as there was sufficient toluene to allow for removal of all the acetic acid and all the water present. The rate of distillation also appeared to be unimportant. The toluene azeotropes could be distilled off as rapidly as the stillhead allowed. It was important not to distill off all the toluene to protect the product from decomposition.

General Procedure. The ligand, if a solid, was ground in a mortar as was the metal acetate. For divalent, trivalent, and tetravalent metal ions, 0.02 mole, 0.03 mole, and 0.04 mole respectively, of ligand were used per 0.008 mole of metal acetate. The ligand, the metal acetate, and 125 ml. of toluene were mixed and heated with stirring (magnetic stirrer) until 100 ml. of toluene was distilled off. At this point, if the product was soluble in toluene, the solution was filtered, and the filtrate concentrated. The product either crystallized or could be induced to crystallize by the addition of ligroin to the concentrate. If the product was insoluble in toluene, it was removed by filtration and recrystallized in an appropriate solvent system where practicable.

Where metal salts other than the acetate were employed, the desired molar quantity of the salt was dissolved in water and the solution treated with aqueous ammonia until precipitation was complete. The precipitate was

centrifuged and washed three times with water in the centrifuge tube. The precipitate was then dissolved in hot glacial acetic acid and this solution mixed with the ligand and the toluene. The procedure employed at this point was the same as that previously employed except that sufficient toluene had to be employed to allow removal of the somewhat larger quantities of acetic acid present. When the distillate no longer contained acetic acid, the previously employed isolation procedures were followed.

ACKNOWLEDGMENT

We are indebted to the Research Corp. for support of this work.

LITERATURE CITED

- (1) Azeotropic Data, *Advan. Chem. Ser.* 6, 253 (1952).
- (2) Coll, C., Mila, A., Pascual, J., *Publs. inst. quim. Alonso Barba (Madrid)* 10, 193 (1956); *CA* 51, 12860c (1956).
- (3) Ginsberg, H.F., Lederman, K., Papa, D., *J. Am. Chem. Soc.* 75, 4587 (1953).
- (4) Handbook of Chemistry, N.A. Lange, ed., pp. 1531, 1537, Handbook Publishers, Sandusky, Ohio, 1952.

RECEIVED for review March 18, 1964. Accepted April 14, 1964.