solution was *colorless*. Because the resultant precipitate contained ammonia which was lost easily, an attempt was made to determine how nearly quantitative this reaction was. Nickel(II) nitrate "6" hydrate (15.2902 g.), which had lost a small portion of its water of crystallization, was dissolved in distilled water (100 ml.) and then treated with concentrated aqueous ammonia (40 ml.). To the resulting dark blue solution, acetylacetone (20 ml.) was added slowly and a light blue precipitate formed leaving a colorless solution. After drying in an atmosphere of ammonia, the weight of the precipitate was 15.4481 g. If the nickel nitrate-6 hydrate had been of stoichiometric composition, the amount of $Ni(C_5H_7O_2)_2 \cdot 2NH_3$ for quantitative precipitation of the nickel would be 15.2996 g. *Anal.* Calcd. for $Ni(C_5H_7O_2)_2 \cdot 2NH_3$: Ni, 20.17; C, 41.27; H, 6.93; N, 9.63. Found: Ni, 20.03; C, 41.13; H, 6.77; N, 8.64. This compound loses ammonia on standing and is converted into the well-characterized green compound, $Ni(C_5H_7O_2)_2$.

Other Reactions.—Attempts to carry out similar reactions with tungstate, chromite and silicate solutions failed completely. The solid reaction products in these cases were the hydrous oxides or hydroxides.

Reactions in basic conditions were examined with $Cd(NH_3)_4{}^{+2}$, $Zn(NH_3)_4{}^{+2}$, $La(CO_3)_x{}^{+3-2x}$, $UO_2(CO_3)_y{}^{-2-2y}$ and $Co(NH_3)_6{}^{+2}$. The reaction between $Ce(NO_3)_6{}^{-2}$ and acetylacetone in acidic solution was also investigated. In all of these instances the products obtained contained varying amounts of basic materials. The conditions and products of these reactions are summarized in Table I.

The precipitate formed with uranium was recrystallized from chloroform and analyzed. It was found to contain 46.7% U and consisted predominantly of bis-(2,4-pentanediono)-dioxouranium(VI) and a small amount of impurity. Since practically the whole of this material was readily soluble in chloroform, the separation of the complex from the basic materials could be assured.

The oxidation products obtained with the Ce(IV) reaction accompanied the complex when it was recrystallized from chloroform. Although the material was very dark in color, its analysis corresponded closely with that expected for the Ce(III) complex rather than the Ce(IV) complex. This material contained 32.9% Ce and the theoretical value for $Ce(C_5H_7O_2)_3$ is 32.0% Ce.

TABLE I

REACTIONS OF ACETYLACETONE WITH SOME COMPLEX IONS

Ion	Soln, expected product		*Anal.*, %
$Cd(NH_3)_4{}^{+2}$	Basic	$Cd(C_5H_7O_2)_2$	
			Calcd. Cd, 36.2; C, 38.7; H, 4.54
			Found Cd, 33.9; C, 32.65; H, 5.22
$Zn(NH_3)_4{}^{+2}$	Basic	$Zn(C_5H_7O_2)_2$	
			Calcd. Zn, 24.8; C, 45.6; H, 5.35
			Found Zn, 39.2; C, 41.71; N, 5.70
$La(CO_3)^{+3-2x}$	Basic	$La(C_5H_7O_2)_3$	
			Calcd. La, 31.8
			Found La, 39.9
$UO_2(CO_3)_y{}^{+2-2y}$	Basic	$UO_2(C_5H_7O_2)_2$[a]	
			Calcd. U, 48.9
			Found U, 43.2 to 50.8
$Co(NH_3)_6{}^{+2}$	Basic	$Co(C_5H_7O_2)_2$	
			Calcd. Co, 22.9; C, 46.7; H, 5.48
			Found Co, 19.2; C, 38.57; H, 6.93
$Ce(NO_3)_5{}^{-2}$	Acidic	$Ce(C_5H_7O_2)_3$[b]	
			Calcd. Ce, 32.8
			Found Ce, 30.8 to 33.8

[a] Acetylacetone dissolves in a solution of the uranyl carbonate complex without causing any precipitation. Only after a considerable amount of acid has been added to this solution does a precipitate begin to form. The final precipitate was obtained from a solution that was still slightly basic, however. [b] When acetylacetone is added to a solution of ammonium hexanitratocerate(IV), an initial reaction produces the dark blood-red tetrakis-(2,4-pentanediono)-cerium(IV). The reduction of the cerium(IV) by the acetylacetone soon occurs, however, to give a very pale yellow solution. When the *p*H of this solution is raised by the slow addition of aqueous ammonia, a light yellow precipitate is obtained and it is this latter material to which the table entries refer.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Inner Complex Chelates. II. Analogs and Polar Substituted Analogs of Bisacetylacetoneëthylenediimine and its Metal Chelates[1,2]

BY RICHARD J. HOVEY, JOHN J. O'CONNELL AND ARTHUR E. MARTELL

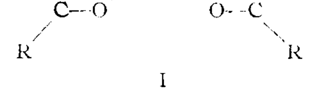
RECEIVED DECEMBER 27, 1958

The syntheses of tetradentate chelating agents of the Schiff base type containing such polar groups as *p*-bromophenyl, *m*-nitrophenyl and trifluoromethyl, and the preparation of some of the corresponding metal chelates of Cu(II), Co(II), Ni(II) and V(IV) are described. The tendency of the imino groups in the ligands to be hydrolytically cleaved is decreased by the presence of phenyl or substituted phenyl groups and by chelation of the ligands with metal ions. Benzene complexes of bisdibenzoylmethaneoxovanadium(IV) and of bisbenzoylacetonepropylenediiminoöxovanadium(IV) are described.

The first paper[3] in this series described the syntheses and properties of several analogs of bisacetylacetone-ethylenediimine and their metal chelates. This work has now been extended and includes many derivatives of the parent compound containing highly polar groups such as *p*-bromophenyl, *m*-nitrophenyl and trifluoromethyl. In subsequent investigations the dipole moments of these ligands and metal chelates will be studied in the light of the information already available on the simpler unsubstituted Schiff bases and their metal chelates.[4]

Results

The compounds which have been synthesized are listed in Table I and may be represented by formula I. In the formula B is the alkyl (or aryl) radical of the diamine and R stands for various polar and non-polar groups. As far as it is known none of the metal chelates listed in Table I has been reported previously; the preparation of three ligands listed in the table, *i.e.*, the propylenediamine Schiff bases



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[1] This work was sponsored by the Office of Ordnance Research under Contract No. DA-19-020-ORD-3243.

[2] Abstracted in part from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, THIS JOURNAL, **77**, 5820 (1955).

[4] P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 264, 2106 (1956).

TABLE I

Name of ligand	B	R	Metal chelates
Bisbenzoylacetonepropylenediimine	$CH(CH_3)CH_2$	C_6H_5	VO(IV)
Bis-*m*-nitrobenzoylacetonepropylenediimine	$CH(CH_3)CH_2$	*m*-$C_6H_4NO_2$	Cu(II), Ni(II)
Bis-*p*-bromobenzoylacetonepropylenediimine	$CH(CH_3)CH_2$	*p*-C_6H_4Br	Ni(II), Co(II)
Bistrifluoroacetylacetonepropylenediimine	$CH(CH_3)CH_2$	CF_3	Ni(II)
Bis-*m*-nitrobenzoylacetonetrimethylenediimine	$(CH_2)_3$	*m*-$C_6H_4NO_2$	Cu(II)
Bistrifluoroacetylacetonetrimethylenediimine	$(CH_2)_3$	CF_3	
Bisacetylacetonetetramethylenediimine	$(CH_2)_4$	CH_3	Cu(II)
Bisbenzoylacetonetetramethylenediimine	$(CH_2)_4$	C_6H_5	Cu(II)
Bis-*m*-nitrobenzoylacetonetetramethylenediimine	$(CH_2)_4$	*m*-$C_6H_4NO_2$	Cu(II)
Bisbenzoylacetonepentamethylenediimine	$(CH_2)_5$	C_6H_5	Cu(II)
Bisbenzoylacetone-1,3-diimino-2-propanol	$CH_2CH(OH)CH_2$	C_6H_5	Cu(II), Ni(II)
Bisacetylacetone-*m*-phenylenediimine	*m*-C_6H_4	CH_3	Cu(II)
Bisbenzoylacetone-2,2′-diiminodiethylamine	$C_2H_5NHC_2H_5$	C_6H_5	Cu(II)

of benzoylacetone, *p*-bromobenzoylacetone and trifluoroacetylacetone, have been reported earlier.[3]

The formation of the Schiff base ligands occurred quite rapidly with the evolution of a considerable amount of heat. In most cases the condensations involving benzoylacetone or benzoylacetone derivatives were carried out successfully in alcohol medium. In the formation of bis-*p*-bromobenzoylacetonepropylenediimine, as well as bis-*m*-nitrobenzoylacetonepropylenediimine, it was necessary to add the diamine directly to the molten diketone. The difficulty in isolating these products from ethanol undoubtedly reflects the much greater solubility of the propylenediamine derivatives noted previously.[3] With regard to the Schiff bases of acetylacetone and trifluoroacetylacetone, optimum yields were obtained by adding the diamine directly to an excess of the diketone.

The crude ligands tend to decompose and frequently become colored on standing. In general the benzoylacetone derivatives were more stable than those derived from acetylacetone and trifluoroacetylacetone. Bisacetylacetonetetramethylenediimine decomposed very rapidly, and a stable product could be obtained only by immediate recrystallization from cyclohexane. The pentamethylene analog could not be purified. The Schiff bases derived from the combination of trifluoroacetylacetone, and of acetylacetone,[3] with trimethylenediamine, were also somewhat unstable.

With the exception of the oxo-vanadium (IV) complexes and bisbenzoylacetonepentamethylenediiminocopper(II), the metal chelates were prepared directly from the Schiff base ligand and the corresponding metal acetate. The use of metal acetates is preferred to the use of metal hydroxides since the acetates remain in solution and the metal chelate, which usually precipitates during the course of the refluxing period, is not contaminated with inorganic impurities.

Discussion

The instability of the ligands is due mainly to the tendency toward hydrolytic cleavage of the imino group. Kinetic measurements on the hydrolysis of azomethines[5] have shown that there is a direct relationship between the rate of hydrolysis and the basicity of the Schiff base. Since the basicity of a Schiff base is primarily dependent on the basicity of the amine from which it is derived, the observation that activation energies for the hydrolysis reactions decrease with increasing basic strength of the amine is perhaps to be expected. It is interesting to note that the diamines used in the present work fall into two catagories: (1) those which have low pK[6] values and form correspondingly stable Schiff bases, such as propylenediamine ($pK = 7.10$ at 25°) and ethylenediamine ($pK = 7.22$ at 20°); and (2) those with higher pK's which form correspondingly less stable Schiff bases with acetylacetone and trifluoroacetylacetone, such as trimethylenediamine ($pK = 8.88$ at 20°), putrescine ($pK = 9.61$ at 20°) and cadaverine ($pK = 10.02$ at 20°).[7]

The greater stability of the benzoylacetone and substituted benzoylacetone derivatives is most likely due to an increase of resonance energy in the system brought about by the presence of the aromatic groups.

Two alternate conformations should be considered for the Schiff bases and metal chelates derived from *p*-bromobenzoylacetone, *m*-nitrobenzoylacetone and trifluoroacetylacetone; *i.e.*, one in which the polar groups are adjacent to the diimine bridge and one in which these groups are in the terminal positions. The latter conformation, which has been assumed for all the ligands and metal chelates of this type listed in Table I, is supported by spectral evidence and dipole moment measurements which will be described in a later publication.

While the Schiff base ligands themselves are somewhat unstable, the corresponding metal chelates are in general quite stable toward hydrolysis. Eichhorn and Marchand[8] similarly observed that the coördination of copper with salicylalglycine resulted in a stabilization of the double bond under conditions which would normally promote its rupture in the absence of the metal ion, *i.e.*, in solutions of low pH. On the other hand Eichhorn and Trachtenberg[9] found that copper(II) and

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(5) B. A. Porai-Koshits, E. M. Pazznaskaya, V. S. Shevchenko and L. A. Pavlova, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1774 (1947); *C. A.*, **42**, 58631 (1948).

(6) K refers to $[HL^+][H^+]/[H_2L^{++}]$ where L is the amine. A similar correlation applies to the dissociation of the second hydrogen ion from the diamine salt.

(7) J. Bjerrum, G. Schwarzenbach and L. Sillen, "Stability Constants," Part I, Organic Ligands, The Chemical Society (London), Burlington House, London, W.T., 1957.

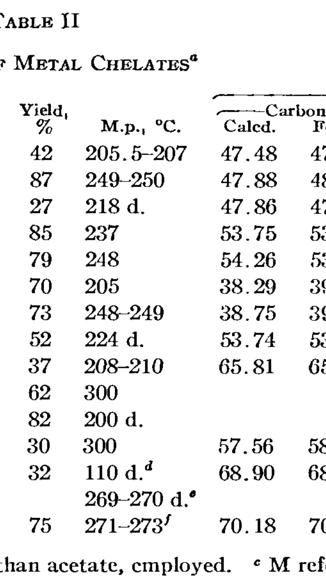
(8) G. L. Eichhorn and N. D. Marchand, THIS JOURNAL, **78**, 2688 (1956).

(9) G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954).

nickel(II) catalyzed the hydrolysis of bis-(2-thiophenal)-ethylenediimine. Also, in the present work it was found that the copper chelate of bisacetylacetonetetramethylenediimine dissolved readily in hot water; upon cooling the solution the characteristic bright blue crystals of copper acetylacetonate were obtained.

These two antithetical influences of the metal ion are most likely due to the difference in stabilities of the chelates formed. Thus the increased acceptor activity of the imine carbon resulting from coördination of the nitrogen atom with the metal ion would be counteracted by stabilization of the chelate compound by resonance or by some special structural feature.

The tarry or resinous products obtained when copper acetate reacts with ligands such as bisbenzoylacetonepentamethylenediimine and bisbenzoylacetone-2,2′-diiminodiethylamine are assumed to be polymeric (*cf.* II). Presumably the length of the diimine bridge renders the formation of a monomeric chelate less probable.



II, Bisbenzoylacetonepentamethylenediiminocopper (II)

The vanadyl chelates of bisbenzoylacetonepropylenediimine and dibenzoylmethane, when purified by recrystallization from benzene, were obtained as solvates which differed markedly from the unsolvated material in color, crystalline form, and other properties. The elementary analysis of bisbenzoylacetonepropylenediimino - oxovanadium(IV), indicated coördination with a single mole of benzene, as is shown in the table

	Analyses, % C	H	N
Calcd. for $C_{23}H_{24}N_2O_2Cu$	64.63	5.66	6.56
Found	68.71	5.84	5.52
Calcd. for $C_{23}H_{24}N_2O_2Cu \cdot C_6H_6$	68.90	5.98	5.54

Also, thermal desolvation of 0.0852 g. of the solvate resulted in a weight loss of 0.0131 g., which compares well with the theoretical value of 0.0132 g.

While Jones[10] has shown by ebullioscopic measurements that bisacetylacetono-oxovanadium(IV) and bisbenzoylacetono-oxovanadium(IV) involve a coördination number of five for vanadium(IV), other β-diketone chelates of the vanadyl ion were found to include one water molecule in the coördination sphere of the metal. Rather similar complexes are formed as lakes by the interaction of VO^{+2} with hydroxyazo and aminoazo dyes; they are fairly stable and all are six-covalent.[11] In

TABLE II

SYNTHESIS OF METAL CHELATES[a]

Ligand	Metal	Reaction solvent	Recrystn. medium	Yield, %	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	M[c] Calcd.	M[c] Found
Bis-*p*-bromobenzoylacetonepropylenediimine	Cu(II)[b]	Acetone	Acetone	42	205.5–207	47.48	47.59	3.81	3.71	4.82	4.20	10.92	10.72
Bis-*p*-bromobenzoylacetonepropylenediimine	Ni(II)	EtOH	EtOH	87	249–250	47.88	48.03	3.84	4.12	4.86	4.80	27.7	28.0
Bis-*p*-bromobenzoylacetonepropylenediimine	Co(II)	MeOH	Benzene	27	218 d.	47.86	47.66	3.84	4.85	4.85	4.66		
Bis-*m*-nitrobenzoylacetonepropylenediimine	Cu(II)	$CHCl_3$	$CHCl_3$–MeOH	85	237	53.75	53.94	4.31	4.21	10.90	11.20		
Bis-*m*-nitrobenzoylacetonepropylenediimine	Ni(II)	$CHCl_3$	$CHCl_3$–MeOH	79	248	54.26	53.97	4.36	4.44	11.01	11.40		
Bistrifluoroacetylacetonepropylenediimine	Cu(II)	EtOH	EtOH	70	205	38.29	39.00	3.46	3.80	6.87	7.10	15.58	14.91
Bistrifluoroacetylacetonepropylenediimine	Ni(II)	EtOH	EtOH	73	248–249	38.75	39.62	3.50	3.96	6.95	7.45		
Bis-*m*-nitrobenzoylacetonetrimethylenediimine	Cu(II)	EtOH	$CHCl_3$–acetone	52	224 d.	53.74	53.97	4.31	4.44	10.90	10.40		
Bisbenzoylacetonetetramethylenediimine	Cu(II)	EtOH	Acetone	37	208–210	65.81	65.67	5.98	6.10	6.40	6.14		
Bisbenzoylacetone-1,3-diimino-2-propanol	Cu(II)	EtOH	Benzene	62	300					6.37	5.62		
Bisbenzoylacetone-1,3-diimino-2-propanol	Ni(II)	EtOH	Benzene	82	200 d.					6.44	6.00	13.49	13.09
Bisacetylacetone-*m*-phenylenediimine	Cu(II)	EtOH	$CHCl_3$	30	300	57.56	58.04	5.43	5.65	8.39	8.30		
Bisbenzoylacetonepropylenediimine	VO(IV)	EtOH	Benzene	32	110 d.[d] 269–270 d.[e]	68.90	68.71	5.98	5.84	5.54	5.52		
Dibenzoylmethane	VO(IV)	EtOH	Benzene	75	271–273[f]	70.18	70.14	4.32	4.68				

[a] General procedure employed unless otherwise noted. [b] Metal hydroxide, rather than acetate, employed. [c] M refers to metal in column 2. [d] Contains one mole of benzene. [e] Desolvated. [f] Previously desolvated at 110°.

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(10) M. M. Jones, THIS JOURNAL, **76**, 5995 (1954).

(11) H. D. K. Drew and F. G. Dunton, *J. Chem. Soc.*, 1064 (1940).

cases where a coördination number of five has been observed for vanadium(IV), the chelates in question were found to add quite readily an additional monodentate donor group such as pyridine and methylamine. The two vanadyl chelates reported here are the first instances in which a benzene molecule is observed to complete the coördination requirement of this metal, although solvents other than water, such as chloroform, have been known to form stable adducts with vanadyl complexes.[12] In view of the symmetry of the benzene molecule the structure suggested for the solvate of bisbenzoylacetonepropylenediimino-oxovanadium(IV) is indicated in Fig. 1 as a π-complex in which the metal ion is coördinated symmetrically with the π-electrons of the aromatic ring.

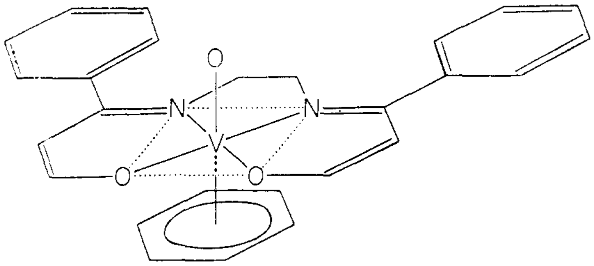

Fig. 1.—Arrangement of ligands in bisbenzoylacetonepropylenediiminooxovanadium(IV).

Experimental

Bis-*m*-nitrobenzoylacetonepropylenediimine.—A 15-g. sample (0.07 mole) of *m*-nitrobenzoylacetone (m.p. 115–115.5°), prepared by the method of Burgress,[13] was heated at 120–130° with 6.5 ml. (0.07 mole) of propylenediamine until completion of the reaction and was crystallized first from ethanol and finally from a mixture of methanol and chloroform. A 50% yield of bright yellow crystals melting in the range 187–188° was obtained.

Anal. Calcd. for $C_{23}H_{24}O_6N_4$: C, 61.05; H, 5.35; N, 12.4. Found: C, 60.60; H, 5.19; N, 12.1.

Bis-*m*-nitrobenzoylacetonetrimethylenediimine.—A 2.0-g. sample (0.01 mole) of *m*-nitrobenzoylacetone was heated with 0.6 ml. (0.005 mole) of trimethylenediamine in 25 ml. of ethanol. Successive recrystallizations from ethanol and benzene resulted in the isolation of an 18% yield of yellow needles melting in the range 137.5–138.5°. The product decomposes slowly when heated.

Anal. Calcd. for $C_{23}H_{24}O_6N_4$: C, 61.05; H, 5.35; N, 12.35. Found: C, 61.16; H, 5.43; N, 12.0.

Bisacetylacetonetetramethylenediimine.—A mixture of 75 ml. (0.7 mole) of acetylacetone and of 15 g. (0.17 mole) of putrescine was allowed to stand overnight. Filtration of the crystalline product from the cooled mixture, and then recrystallization from cyclohexane, gave 25 g. (58% of the theoretical amount) of yellow plates melting at 105.5–106.6°. The impure product is unstable but the recrystallized material may be stored indefinitely without decomposition.

Anal. Calcd. for $C_{14}H_{24}O_2N_2$: C, 66.63; H, 9.59; N, 11.10. Found: C, 66.48; H, 9.32; N, 10.70.

Bisbenzoylacetonetetramethylenediimine.—A solution of 81 g. (0.5 mole) of benzoylacetone and 22 g. (0.25 mole) of putrescine in 150 ml. of ethanol was heated. After the reaction had ceased, the mixture was cooled, and the product which crystallized was recrystallized from benzene. The yield of colorless needles, melting at 137.5–138.5°, was 80 g. or 85% of the theoretical amount.

Anal. Calcd. for $C_{24}H_{26}O_2N_2$: C, 76.56; H, 7.50; N, 7.44. Found: C, 76.99; H, 7.59; N, 7.10.

Bis-*m*-nitrobenzoylacetonetetramethylenediimine.—A solution of 4 g. (0.02 mole) of *m*-nitrobenzoylacetone and 1.5 ml. (0.01 mole) of putrescine in 30 ml. of ethanol was refluxed for a short time, cooled, and the product was recrystallized from a mixture of ethanol and chloroform. The yield of pale yellow granular crystals, melting at 205–206°, was 30% of the theoretical amount.

Anal. Calcd. for $C_{24}H_{26}O_6N_4$: C, 61.79; H, 5.62; N, 12.01. Found: C, 61.56; H, 5.66; N, 12.0.

Bisbenzoylacetonepentamethylenediimine.—A solution of 28 g. (0.17 mole) of benzoylacetone and 10 ml. (0.08 mole) of cadaverine in 200 ml. of methanol was refluxed for a short time and then allowed to stand at room temperature. The colorless crystalline product was recrystallized from acetone. The yield of purified material, which melted at 137°, was 22 g. or 65% of the theoretical amount.

Anal. Calcd. for $C_{25}H_{30}O_2N_2$: C, 76.89; H, 7.74; N, 7.17. Found: C, 77.15; H, 7.80; N, 7.04.

Bisbenzoylacetone-1,3-diimino-2-propanol.—A solution of 50 g. (0.03 mole) of benzoylacetone and 20 ml. of molten 1,3-diamino-2-propanol in 150 ml. of ethanol was heated until visible signs of the reaction had ceased. The product which separated from the cooled reaction mixture was obtained as colorless fibrous crystals after recrystallization from benzene. The yield was 23 g. or 40% of the theoretical amount.

Anal. Calcd. for $C_{23}H_{26}O_3N_2$: C, 72.99; H, 6.92; N, 7.40. Found: C, 73.00; H, 6.73; N, 7.06.

Bisacetylacetone-*m*-phenylenediimine.—A solution of 9.0 g. (0.05 mole) of *m*-phenylenediamine and 10 ml. (0.1 mole) of acetylacetone in 40 ml. of ethanol was refluxed for one day. The product which separated from the cooled reaction mixture was recrystallized once from acetone and twice from benzene. The final yield of purified material was 25% of the theoretical amount.

Anal. Calcd. for $C_{16}H_{20}O_2N_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.89; H, 7.39; N, 10.00.

Bisbenzoylacetone-2,2′-diiminodiethylamine.—A solution of 50 g. (0.3 mole) of benzoylacetone and 18 ml. (0.1 mole) of diethylenetriamine in 150 ml. of ethanol was heated until visible indications of the reaction had ceased. The product which crystallized out of the strongly cooled reaction mixture was recrystallized from ethanol. The final yield of purified material, melting in the range of 105.5–106.5°, was 27% of the theoretical value.

Anal. Calcd. for $C_{24}H_{29}O_2N_3$: C, 73.63; H, 7.47; N, 10.73. Found: C, 73.29; H, 7.61; N, 11.00.

Synthesis of Metal Chelates.—In the synthesis of most metal chelates of the Schiff bases, slightly more than the stoichiometric amount of the metal acetate was added to the appropriate ligand, usually, but not always, dissolved in ethanol. Although a color change indicating complex formation usually began immediately, completion of the reaction as evidenced by precipitation of the metal chelate required from a few minutes to several hours, depending on the ligand. Purification was accomplished by recrystallization from a variety of non-aqueous solvents. The experimental details are given in Table II.

WORCESTER, MASS.

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[12] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

[13] H. Burgress, *J. Chem. Soc.*, 2017 (1937).