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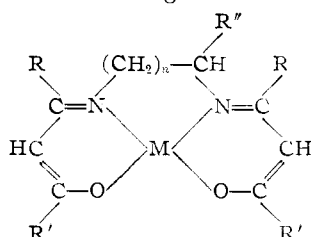
Inner Complex Chelates. I. Analogs of Bisacetylacetonethylenediimine and its Metal Chelates^{1,2}

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Syntheses of bisacetylacetonethylenediimine, bisacetylacetonepropylenediimine, bistrifluoroacetylacetonethylenediimine, bistrifluoroacetylacetonepropylenediimine, bisbenzoylacetonethylenediimine, bisbenzoylacetonepropylenediimine, bis-*p*-bromobenzoylacetonepropylenediimine, bisacetylacetonetrimethylenediimine, bisbenzoylacetonetrimethylenediimine, and the preparation of some of the corresponding chelates of Cu(II), Co(II), Ni(II), Pt(II), and Pd(II) are described. The probable structures of the metal chelates are discussed in the light of the properties of the compounds and the coordination requirements of the metal ions.

In connection with research projects being conducted in these laboratories on dipole moments and infrared spectra of metal chelate compounds related to synthetic and natural oxygen carriers, it was decided to prepare as model substances, a series of tetradentate chelated compounds with the simplest possible structure, and with the smallest possible number of polar groups. Metal chelates classifiable under general formula I were considered to meet these requirements as well as possible for a single closely-related class of compounds. The resonating ring system is identical with that of the synthetic cobalt(II) chelate oxygen carriers, without the additional benzene rings.



(I) Metal chelate compounds derived from bisacetylacetonethylenediimine

In the parent substances (bisacetylacetonethylenediimine chelates) the molecular weight is as small as conceivably possible in tetradentate chelate compounds.

Very few examples of this type of compound have been prepared previously. The parent ligand, bisacetylacetonethylenediimine, and its Cu(II) chelate, were first prepared by Combes and Combes,³ and studied later by Schwarzenbach and Litz.⁴ The Cu(II), Co(II), Ni(II) and Pd(II) chelates were prepared by Morgan and Smith,⁵ the copper chelate has since been studied by a number of investigators.^{6,7} The ligand derived from benzoylacetonethylenediimine has been prepared by Frost.⁸ Ligands obtained by the condensation

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(2) Abstracted in part from a dissertation submitted by Paul J. McCarthy to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A. Combes and C. Combes, *Compt. rend.*, **108**, 1252 (1889).

(4) G. Schwarzenbach and K. Litz, *Helv. Chim. Acta*, **23**, 1139 (1940).

(5) (a) G. Morgan and J. Smith, *J. Chem. Soc.*, 2030 (1925); (b) 918 (1926).

(6) (a) R. Duffield and M. Calvin, *THIS JOURNAL*, **68**, 557 (1946);

(b) P. Ray and D. N. Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).

(7) V. Rügheimer, *Ber.*, **47**, 2764.

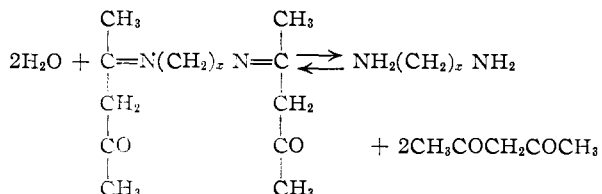
(8) A. Frost, Versenes, Inc., Framingham, Mass., private communication.

of ethylenediamine and trimethylenediamine with acetylacetonethylenediimine, and trifluoroacetylacetonethylenediimine, and the corresponding Cu(II) chelates have been prepared by Martell, Belford and Calvin⁹ for the purpose of studying absorption spectra.

Results

The metal chelate compounds prepared in this investigation are summarized in Table I. The symbols designate the atoms or atomic groupings indicated in Formula I. The ligands may also be considered as included in general formula I, if the metals were replaced by two hydrogen ions.

The condensation of ethylenediamine with the β -diketones, particularly acetylacetonethylenediimine, and trifluoroacetylacetonethylenediimine, was found to be highly exothermic when anhydrous reagents were employed. Nevertheless the Schiff bases obtained by the condensation of ethylenediamine and trimethylenediamine with acetylacetonethylenediimine were found to dissociate in water, according to the equilibrium



The Schiff base obtained from 1,3-diaminopropane seemed less stable than the ethylenediamine derivative, but both products seemed to retain a faint amine odor for some time. As one would expect from the strongly basic nature of the diamines, the above equilibrium is shifted to the right in the presence of mineral acids.

Two general methods were employed for the preparation of the metal chelate from the corresponding ligand: 1, heating of the freshly-prepared metal hydroxide with a solution of the ligand in an organic solvent, and 2, heating of a hydrated inorganic salt of the metal with the stoichiometric amount of base and ligand, according to the procedure given by Morgan and Smith.⁵ The former procedure involved milder conditions and seemed to give more satisfactory results. The first method failed to give a Ag(II) chelate from Ag(II) oxide prepared by the method of Hammer and Kleinberg.¹⁰ The resulting extensive decomposition and

(9) A. E. Martell, L. Belford, and M. Calvin, unpublished work.

(10) R. Hammer and J. Kleinberg, in "Inorganic Syntheses," Vol. IV, J. Bailar, Jr., Editor, McGraw-Hill Book Co., New York, N. Y., 1953, p. 12.

TABLE I
METAL CHELATE COMPOUNDS DERIVED FROM BISACETYLACETONE-ETHYLENEDIIMINE

Name of ligand, ^a diimine	n	R	R'	R''	M(II)
Bisacetylaceton-ethylene	1	CH ₃	CH ₃	H	Cu, Ni, Co, Pd, Pt
Bisacetylacetonpropylene	1	CH ₃	CH ₃	CH ₃	Cu, Ni
Bistrifluoroacetylaceton-ethylene	1	CH ₃	CF ₃	H	Cu
Bistrifluoroacetylacetonpropylene	1	CH ₃	CF ₃	CH ₃	Cu
Bisbenzoylaceton-ethylene	1	C ₆ H ₅	CH ₃	H	Cu, Ni, Co
Bisbenzoylacetonpropylene	1	C ₆ H ₅	CH ₃	CH ₃	Cu, Ni, Co
Bis- <i>p</i> -bromobenzoylacetonpropylene	1	<i>p</i> -C ₆ H ₄ Br	CH ₃	CH ₃	Cu
Bisacetylacetontrimethylene	2	CH ₃	CH ₃	H	Cu
Bisbenzoylacetontrimethylene	2	C ₆ H ₅	CH ₃	H	Cu

^a Non-systematic names are used first, since they indicate both structure and method of preparation, and secondly, because the I.U.C. and *Chem. Abstracts* nomenclature is more complicated (*e.g.*, in place of bisacetylaceton-ethylenediimine, one would have 4,4'-(ethylenediimino)-di-3-penten-2-ol).

polymerization of the organic ligand indicated that the difficulty was probably due to the oxidizing action of the silver oxide. It was also found that the zinc(II) and cadmium(II) chelates failed to form from the hydroxide by the method of preparation employed in this investigation.

Discussion

For all the metal chelates listed in Table I, the analyses showed that no coordinating groups were present in the final, dried, products except for the binegative ligand anion itself. The ligands apparently supply a maximum of four coordinate bonds, and in the case of the ethylenediimine and propylenediimine derivatives, these bonds are strongest when they all lie in the same plane, which is also the plane of the two conjugated 6-rings. Thus it seems that all resulting chelates involve a characteristic coordination number of four for the metal ion, and that all structures are square-planar. This conclusion is further supported by the fact that in the few cases where hydrates were obtained, the water was driven off under relatively mild conditions ($\sim 100^\circ$). Also the relatively high solubility of the chelates in non-polar and low-polarity solvents indicates an absence of strong metal-metal interactions between the chelate molecules. In this connection it is interesting to note that Morgan and Smith⁴ considered the monohydrate of bisacetylaceton-ethylenediimino Cu(II) to indicate a coordination number of five for divalent copper. Also, they considered that molecular association of the nickel(II) and palladium(II) chelates with ethylenediimine and chloroform indicated the possibility of higher coordination numbers for these metals. In all cases, however, the addition groups cannot be considered as more than weakly bound, since they were removed readily under mild conditions. Examples of coordination number six for Cu(II) and Ni(II), and of five for Cu(II), are well known. For these two metals, therefore, the loosely-bound additional donors may be associated with the metal, or may alternatively be considered to form a loose molecular (or crystal lattice) compound with the chelate.

Although the ligands themselves are Schiff bases which are somewhat susceptible to hydrolysis, the metal chelates, particularly those of Cu(II), Ni(II) and Pd(II), are quite stable toward hydrolysis. This is contrary to Cu(II) and Ni(II) catalysis of the hydrolysis of Schiff bases such as bis-(2-thio-

phenal)-ethylenediimine.¹¹ The difference is no doubt due to the instability of the bis-(2-thiophenyl)-ethylenediimine chelates, in contrast to the stability of the chelate formed by hydrolysis. On the other hand, the Schiff bases derived from acetylaceton and its analogs form metal chelate compounds which are themselves initially very stable. This high stability is probably due to polarization of the ligand electrons by the metal ion, and to the participation of the metal in the π -bond systems of the two coordinated conjugated rings. Figure 1 shows how the unfilled d-orbital of Cu(II) is the center of a π -bond system encompassing 11 atoms. Such a highly stable structure is favored by coplanarity of the metal chelate rings.

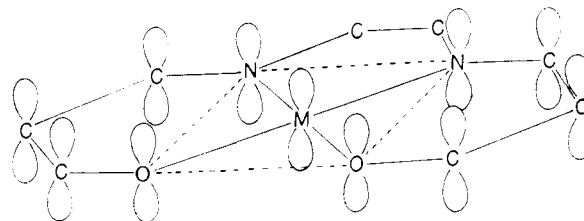


Fig. 1.—The π -bond system of the two coordinated conjugated rings.

Experimental

Reagents.—A 57% aqueous solution of ethylenediimine purchased from Dow Chemical Company was dried over solid potassium hydroxide and distilled, the fraction boiling over the range 116 – 117° being used for synthetic work described below. Propylenediimine, obtained from the Matheson Company, and trimethylenediimine, kindly donated by S. Chaberek, Jr., were dried and distilled in the same manner, the final products distilling from 116 – 119° , and 133 – 136° , respectively. Acetylaceton obtained from Distillation Products Industries, and trifluoroacetylaceton, obtained from Peninsular Chemresearch, were found to boil over the ranges 133 – 135° and 106 – 108° , respectively, and were used without further purification. Part of the benzoylaceton was made by a Claisen¹² condensation of acetophenone and ethyl acetate. The remainder, obtained from Mid-continent Chemicals Corporation, had a melting range of 56.0 – 56.5° .

Bisacetylaceton-ethylenediimine.—One mole (60 g.) of anhydrous ethylenediimine was added slowly to two moles of acetylaceton. Considerable heat was evolved during the reaction, with the result that the water formed boiled off. The product solidified on cooling to a straw-colored substance. After two recrystallizations from water and after being dried under reduced pressure, the colorless solid melted

(11) G. L. Eichhorn and I. M. Trachtenberg, *THIS JOURNAL*, **76**, 5183 (1954).

(12) L. Claisen, *Ann.*, **291**, 51 (1896).

from 111–111.5°. It was found to be very soluble in hot water and in many common organic solvents, except petroleum ether and diethyl ether, but to be only moderately soluble in water at 0°. The yield was 135 g., or 60% of the theoretical amount after two recrystallizations.

Anal. Calcd. for $C_{12}H_{20}O_2N_2$: N, 12.5. Found: N, 12.7.

Bisacetylacetonepropylenediimine.—The procedure given above for bisacetylacetonethylenediimine was employed. The product was found to be very soluble in cold and hot water, as well as in many common organic solvents except cold absolute ethyl ether. It was accordingly recrystallized three times from this solvent. The yield of the resulting small, colorless needles which melted at 91° was 60% of the theoretical amount after two recrystallizations.

Anal. Calcd. for $C_{15}H_{22}O_2N_2$: N, 11.8; C, 65.52; H, 9.31. Found: N, 11.7; C, 65.47; H, 9.49.

Bisacetylacetonetrimethylenediimine.—This substance was also prepared in the same way as bisacetylacetonethylenediimine. The resulting straw-colored liquid was heated on a steam-bath about 30 minutes to remove the water formed in the reaction. The compound solidified slowly to long needles. The product could not be dried completely, and no solvent suitable for recrystallization was found. The crude Schiff base was used in the preparation of the copper chelate.

Bisbenzoylacetone-ethylenediimine.—To a solution of 0.5 mole of benzoylacetone in 100 cc. of hot ethanol was added 0.25 mole of anhydrous ethylenediamine. The desired compound began to precipitate after the solution had been boiled about 10–15 minutes. After the reaction mixture had cooled, the precipitate was removed by filtration, and was washed with, and then recrystallized from, ethanol. After the resulting colorless compound was dried at 100°, it was found to melt at 180.5°. At room temperature this ligand was found to be insoluble in water and only slightly soluble in ordinary organic solvents, such as ether, petroleum ether, benzene, acetone, and ethanol. The yield was 70% of the theoretical amount after one recrystallization.

Anal. Calcd. for $C_{22}H_{24}O_2N_2$: N, 8.04; C, 75.83; H, 6.94. Found: N, 7.82; C, 75.96; H, 7.00.

Bisbenzoylacetonepropylenediimine.—This substance was prepared in the same way as bisbenzoylacetone-ethylenediimine. When the reaction mixture was allowed to stand overnight, the compound precipitated slowly as a hard crystalline mass, which was recrystallized twice from ethanol. The resulting colorless compound was dried in the air, then in a vacuum desiccator. It was found to melt over the range 115.5–116°. It is much more soluble in organic solvents than is bisbenzoylacetone-ethylenediimine. The yield was 70% of the theoretical amount after one recrystallization.

Anal. Calcd. for $C_{25}H_{26}O_2N_2$: N, 7.73; C, 76.21; H, 7.23. Found: N, 7.76; C, 76.03; H, 7.25.

Bisbenzoylacetone-trimethylenediimine.—The procedure was the same as that employed for bisbenzoylacetone-ethylenediimine. The product precipitated rapidly when an ethanol solution of the diamine and benzoylacetone was heated 10–15 minutes on a steam-bath. The compound was recrystallized slowly from ethanol to yield colorless, hydrated needles. After two recrystallizations from benzene-petroleum ether, the infrared spectrum still showed the presence of hydroxyl. The compound was vacuum-dried for two days before it was used for the dipole moment measurement. Bisbenzoylacetone-trimethylenediimine was found to darken slightly when dried at 100°, and to melt from 111.5 to 112°. Its solubility is similar to bisbenzoylacetonepropylenediimine. The yield was 70% of the theoretical amount after one recrystallization.

Anal. Calcd. for $C_{28}H_{26}O_2N_2$: N, 7.73; C, 76.2; H, 7.23. Found: N, 7.76; C, 76.3; H, 7.19.

Bistrifluoroacetylacetonethylenediimine.—Two moles of trifluoroacetylacetonone were treated with one mole of anhydrous ethylenediamine in the same manner that was employed in the preparation of bisacetylacetonethylenediimine, except that the reagents were kept at 0° to prevent volatilization of the trifluoroacetylacetonone as the result of the heat of reaction. The product was recrystallized from benzene. The resulting colorless needles were found to be much less soluble in organic solvents than the non-fluorinated compound, and to be completely insoluble in water.

The compound was found to melt at 157°. The yield was 70% of the theoretical amount after two recrystallizations.

Anal. Calcd. for $C_{12}H_{14}F_6O_2N_2$: N, 8.43; C, 43.38; H, 4.25. Found: N, 7.81; C, 43.52; H, 5.18.

Bistrifluoroacetylacetonepropylenediimine.—The procedure employed is the same as that used for the preparation of bistrifluoroacetylacetonethylenediimine. The product was twice recrystallized from ethanol. A 36% yield was obtained. The melting point range was found to be 143.5 to 144.5°.

Anal. Calcd. for $C_{15}H_{16}N_2O_2F_6$: C, 45.09; H, 4.66; N, 8.09. Found: C, 45.52; H, 4.59; N, 7.60.

***p*-Bromobenzoylacetone.**—A 0.05-mole sample of *p*-bromoacetophenone was dissolved in 35 ml. of ethyl ether, which had been previously dried over sodium. This solution was poured into a 200-ml. round-bottom flask containing 0.10 mole of sodium wire. To the solution was added 8.8 ml. (0.10 mole) of ethyl acetate. The reaction is spontaneous and was completed in about 45 minutes. The sodium salt of the diketone was precipitated from the ether solution by the addition of several drops of water with stirring, separated by filtration, allowed to dry in the air, and then dissolved in approximately 200 ml. of hot water. Insoluble resinous substances were separated before acidifying with glacial acetic acid. After recrystallization of the diketone from ethanol, transparent needles, which melted at 92°, were obtained. The yield of pure substance was 4.6 g. (38% of theoretical value).

Anal. Calcd. for $C_{10}H_9O_2Br$: C, 49.82; H, 3.76; Br, 33.2. Found: C, 50.13; H, 3.87; Br, 33.1.

Bis-*p*-bromobenzoylacetonepropylenediimine.—A 0.02-mole sample of *p*-bromobenzoylacetone was melted and 1 ml. (0.01 mole) of propylenediamine was added. Under these conditions the reaction was spontaneous. Recrystallization of the gummy residue from ethanol resulted in the removal of the resinous impurity, and the isolation of a relatively pure sample of the Schiff base. The yield of the off-white crystalline compound, having a melting range of 145–146°, was 2.5 g., or 44% of the theoretical amount.

Anal. Calcd. for $C_{22}H_{24}N_2O_2Br$: C, 53.09; H, 4.65; N, 5.38; Br, 30.7. Found: C, 53.27; H, 4.17; N, 5.10; Br, 31.4.

Preparation of the Metal Chelates.—Unless individual cases are cited to the contrary, the metal chelates were made by the following general procedure: an acetone solution of the appropriate ligand was refluxed with an excess of the appropriate metal hydroxide until the reaction was completed. Except in cases of the copper(II) and nickel(II) chelates of bisbenzoylacetone-ethylenediimine, and the copper(II) chelate of trifluoroacetylacetonethylenediimine, the products were quite soluble in hot acetone, and could be separated by filtration from the unreacted metal hydroxide. Metal chelates containing phenyl groups precipitated readily from their acetone solutions when cooled. Any unreacted ligand was left in solution, since the ligands are more soluble than their chelates. Except where otherwise noted, acetylacetonediimine chelates were precipitated from their acetone solutions by the addition of water. The ligands of these chelates are water-soluble; unreacted ligand therefore remained in solution.

The metal hydroxides were prepared by adding aqueous NaOH to a water solution of the metal chloride (or other soluble salt). The precipitate was filtered and washed free of -OH and the other anion. $Cu(OH)_2$ was found to be more easily filtered and washed if prepared at 0°. In the preparation and washing of $Co(OH)_2$, only freshly-boiled, distilled water should be used, since dissolved oxygen tends to oxidize divalent cobalt to the trivalent state.

In most cases preparation of the metal chelate compounds was found to be nearly quantitative, and approximately the theoretical amount of metal hydroxide was dissolved. The loss resulting from isolation of the solid chelate amounted to 10–15%. Recrystallization usually resulted in an additional 10% loss. Thus the final yield of pure product was 73% for bisacetylacetonethylenediimino-copper(II) and 80% for bisacetylacetonethylenediimino-nickel(II). Cobalt chelates were obtained in much lower yield as a result of oxidation of the ligand in solution.

Bisacetylacetonethylenediimino-copper(II).—About three hours of refluxing were sufficient to complete the reaction. After isolation the compound was recrystallized from

acetone, dried in air, and then dried at 100° for 1–2 hours. The resulting microscopic, dark-purple crystals were found to melt at 141.5° (lit.^{5a} 137°). The compound is very soluble in common organic solvents, but insoluble in water.

Anal. Calcd. for $C_{12}H_{18}O_2N_2Cu$: N, 9.80; Cu, 22.24. Found: N, 10.1; Cu, 22.13.

Bisacetylaceton-ethylenediiminonickel(II).—Six hours of refluxing was found to be desirable. It was recrystallized from an acetone solution containing a small amount of water. The compound is red-brown, and resembles the copper(II) chelate in solubility. The hydrated crystals thus obtained were dried at 100°. The product was found to melt over the range 195–196° (lit.^{5a} 200°).

Anal. Calcd. for $C_{12}H_{18}O_2N_2Ni$: N, 9.97; Ni, 20.89. Found: N, 9.90; Ni, 20.83.

Bisacetylaceton-ethylenediiminocobalt(II).—This compound was prepared according to the method of Morgan and Smith⁴ as well as by the general procedure outlined above. Regardless of the method employed in this preparation, it was not possible to purify the compound satisfactorily because of its rapid decomposition in solution.

Bisacetylaceton-ethylenediiminopalladium(II).—The palladium(II) chelate was prepared by the method of Morgan and Smith.^{5a} The fine, yellow crystals were recrystallized from benzene, dried in air, and then dried at 100° for one hour. They were found to melt at 228° (lit.^{5a} 228°).

Anal. Calcd. for $C_{12}H_{18}O_2N_2Pd$: N, 8.52; C, 43.81; H, 5.52. Found: N, 8.28; C, 44.12; H, 5.75.

Bisacetylaceton-ethylenediiminoplatinum(II).—Several attempts were made to form this chelate; K_2PtCl_4 was used as the starting material. The reaction seems very sensitive to the amount of base present, which should be controlled carefully. When the procedure for preparing the Pd derivative was followed, a small amount of dark-yellow needles was obtained. These decomposed at approximately 247°, and with more rapid heating melted at about 250°.

Anal. Calcd. for $C_{12}H_{18}O_2N_2Pt$: N, 6.71; C, 34.52; H, 4.35. Found: N, 6.83; C, 34.11; H, 4.65.

Bisacetylacetonpropylenediiminocopper(II).—This chelate was prepared by the same procedure as that used for bisacetylaceton-ethylenediiminocopper(II) and was crystallized from acetone solution by the addition of water. It was dried in air and then in a vacuum desiccator. The dark-purple compound thus obtained is very soluble in organic solvents. It was found to melt from 121.5 to 122°.

Anal. Calcd. for $C_{15}H_{20}O_2N_2Cu$: N, 9.34; Cu, 21.20. Found: N, 9.34; Cu, 21.31.

Bisacetylacetonpropylenediiminonickel(II).—Nickel(II) hydroxide was treated with bisacetylacetonpropylenediimine in the same way that was used to prepare bisacetylaceton-ethylenediimino-Ni(II). The product resembles the latter compound in appearance and solubility. It was found to melt from 157 to 157.5°.

Anal. Calcd. for $C_{15}H_{20}O_2N_2Ni$: N, 9.50; Ni, 19.90. Found: N, 9.67; Ni, 19.84.

Bisacetylacetontrimethylenediiminocopper(II).—The crude bisacetylacetontrimethylenediimine was treated with copper(II) hydroxide as in the procedure given for bisacetylaceton-ethylenediiminocopper(II). The compound was readily formed, and less refluxing was necessary than for the latter. After recrystallization from acetone and water, the chelate was obtained in the form of green, microscopic crystals, which melted over the range 119.5–120°. It was found to be very soluble in common organic solvents.

Anal. Calcd. for $C_{18}H_{24}O_2N_2Cu$: N, 9.34; Cu, 21.20. Found: N, 9.16; Cu, 21.41.

Bisbenzoylaceton-ethylenediiminocopper(II).—The acetone solution was refluxed about 24 hours in accordance with the general procedure given above. Because of its very low solubility in acetone, the chelate precipitated as soon as it was formed. It was separated from excess hydroxide by treatment of the mixture with dilute HNO_3 . (Dilute mineral acids decompose the corresponding acetylacetonediimine chelates.) Recrystallization of the compound from chloroform removed any unreacted ligand. The brown-red crystals of the chelate begin to decompose at about 274°. The chelate is practically insoluble at room temperature in ether, ethanol, acetone and water.

Anal. Calcd. for $C_{22}H_{22}O_2N_2Cu$: N, 6.83; Cu, 15.51. Found: N, 6.54; Cu, 15.38.

Bisbenzoylaceton-ethylenediiminonickel(II).—Bisbenzoylaceton-ethylenediimine was converted to the nickel(II) chelate by use of the procedure described above for the corresponding copper(II) chelate. It was recrystallized from a large volume of acetone to yield small, brown-red needles which melted from 288 to 289°. It was found to be slightly soluble in benzene and ether at room temperature, but insoluble in ethanol and water.

Anal. Calcd. for $C_{22}H_{22}O_2N_2Ni$: N, 6.92; Ni, 14.49. Found: N, 7.28; Ni, 14.26.

Bisbenzoylaceton-ethylenediiminocobalt(II).—A small test sample of the compound was made and isolated in the same way as bisbenzoylaceton-ethylenediiminocopper(II), except that refluxing was continued for only 10 hours. The product was recrystallized from acetone-water. The microscopic orange-red crystals thus obtained were found to decompose around 265°.

Anal. Calcd. for $C_{22}H_{22}O_2N_2Co$: N, 6.91; Co, 14.54. Found: N, 6.80; Co, 14.30.

Bisbenzoylacetonpropylenediiminocopper(II).—The reaction mixture was refluxed about 12 hours, and the chelate precipitated when the acetone solution was cooled. After the product had been recrystallized twice from acetone and dried at 100°, it was obtained as dark-green plates which melted from 176.5 to 177°. The compound was found to be much more soluble in acetone and benzene than is bisbenzoylaceton-ethylenediiminocopper(II). It is also somewhat soluble in hot and cold ethanol and ethyl ether.

Anal. Calcd. for $C_{25}H_{24}O_2N_2Cu$: N, 6.61; Cu, 14.99. Found: N, 6.82; Cu, 14.89.

Bisbenzoylacetonpropylenediiminonickel(II).—This substance was prepared and recrystallized in the same way as the corresponding copper(II) chelate, and resembles it in solubility. Recrystallization from acetone yielded bright-red needles which were found to melt at 175°.

Anal. Calcd. for $C_{25}H_{24}O_2N_2Ni$: N, 6.68; Ni, 14.00. Found: N, 6.76; Ni, 14.06.

Bisbenzoylacetonpropylenediiminocobalt(II).—Cobalt(II) hydroxide was treated with bisbenzoylacetonpropylenediimine according to the general procedure except that ethanol was used in place of acetone, and refluxing was continued for about 24 hours to ensure completion of the reaction. The orange-red needles which precipitated from the ethanol solution, when the latter was cooled, were immediately removed by filtration and air-dried. No attempt was made to recrystallize the compound since its solutions darken and decompose rapidly. The chelate was found to decompose at about 265°, and to darken rather quickly even when heated to 80°. It is very soluble in benzene and acetone at room temperature.

Anal. Calcd. for $C_{25}H_{24}O_2N_2Co$: N, 6.68; Co, 14.05. Found: N, 6.51; Co, 14.19.

Bisbenzoylacetontrimethylenediiminocopper(II).—The procedure described for the preparation and purification of bisbenzoylacetonpropylenediiminocopper(II) was employed, except that refluxing was continued for about 24 hours. The small, black crystals thus obtained were found to melt from 181.5 to 182.5°. This chelate was found to dissolve readily in benzene to form a dark-green solution.

Anal. Calcd. for $C_{28}H_{24}O_2N_2Cu$: N, 6.61; Cu, 14.99. Found: N, 6.70; Cu, 14.68.

Bistrifluoroacetylaceton-ethylenediiminocopper(II).—The same procedure as that given for bisacetylaceton-ethylenediiminocopper(II) was employed. The product was formed very readily in part even without refluxing. Much of the compound precipitated in the original acetone solution, and was accordingly separated from unreacted hydroxide by extraction with more hot acetone. It was recrystallized from a large volume of acetone and dried for a few hours at 100°. The fine, purple needles thus obtained sublime at approximately 220°. This chelate was found to be much less soluble in benzene than the non-fluorinated compound.

Anal. Calcd. for $C_{12}H_{12}F_6O_2N_2Cu$: N, 7.12; C, 36.60; H, 3.07. Found: N, 6.94; C, 36.50; H, 3.43.

Bistrifluoroacetylacetonpropylenediiminocopper(II).—The general procedure for the preparation of metal chelates was employed; alcohol, however was used as the solvent. Although the chelate formed partly in the cold, the reaction mixture was refluxed overnight to ensure completion of the reaction. The product was recrystallized once from eth-

anol and dried at 100–110°. A yield of 70% of the theoretical amount was obtained. The light-purple microscopic crystals were found to melt at 205°.

Anal. Calcd. for $C_{12}H_{14}F_8O_2N_2Cu$: C, 38.29; H, 3.46; N, 6.87; Cu, 15.58. Found: C, 39.00; H, 3.80; N, 7.10; Cu, 14.91.

Bis-*p*-bromobenzoylacetonepropylenediiminocopper(II).—The general procedure was followed with acetone as the solvent. The reaction mixture was refluxed for approximately 20 hours. The product, which was recrystallized from acetone, was in the form of brown microscopic crystals which melted at 205.5–207.0°. The compound is fairly soluble in acetone, but only slightly soluble in alcohol and benzene. A 42% yield was obtained.

Anal. Calcd. for $C_{28}H_{20}O_2N_2Br_2Cu$: C, 47.48; H, 3.81;

N, 4.82; Cu, 10.92. Found: C, 47.59; H, 3.71; N, 4.20; Cu, 10.72.

Metal Analyses.—All metal analyses were made in the following manner. The sample was placed in a sealed tube with concentrated HNO_3 and heated in a Carius furnace until completely oxidized. After it had cooled, the tube was opened and the contents were diluted with water and made alkaline with ammonia. The metal was titrated with a solution of disodium salt of ethylenediaminetetraacetic acid, with murexide as the indicator, according to the procedure described by Schwarzenbach.¹³

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The Solution of Cadmium in Liquid Cadmium Chloride

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The melting point depression of cadmium in cadmium chloride has been measured. From the results it is inferred that cadmium probably forms Cd_2^{++} ions on dissolving in liquid cadmium chloride. Related experimental data are discussed and found to support this view. It seems that also in other cases the formation of metal-metal bonds might be responsible for the solubility of a metal in its halides.

Introduction

The solubility of metals in their liquid halides has been subject of much discussion, but the nature of the solutions seems not to be settled yet. Much experimental work is still needed to throw light upon the valence states in question. Unfortunately, large experimental difficulties are encountered in several of the most interesting and technically important systems, as that of aluminum and cryolite.¹ Some systems, like the Cd– $CdCl_2$ system, are easier to deal with, however, and data from these systems might provide a clue to the general problem. Many authors have therefore studied the solution of Cd in $CdCl_2$, but no definite conclusions as to the nature of the solution have been agreed upon.^{2–8}

The cadmium chloride rich part of the Cd– $CdCl_2$ phase diagram for the system Cd– $CdCl_2$ has been investigated by Aten,² Hedger and Terrey,⁷ and Urazow and Karnaukhov⁸ by thermal analysis.

Accurate measurements in this region of the phase diagram can be shown to give strong evidence about the nature of the solution. To get sufficiently accurate data, the liquidus curve has been redetermined by the present authors from 0 to 9.4 mole % metallic cadmium. It will be shown that the experimental data provide support to the view

that Cd_2^{++} ions are present in the liquid. This view is also confirmed by other experimental data.

Experimental

Cadmium chloride of C.P. grade was heated with NH_4Cl and melted in a stream of argon gas before use. The argon was a pure grade commercial preparation from tank origin, purified by passing over copper at 500°, over cupric oxide at 300°, and dried by passing through a calcium chloride, ascarite and phosphorus pentoxide train. A laboratory reagent cadmium metal from "British Drug House" was used.

The primary crystallization temperatures were measured with a Pt–Pt 10% Rh thermocouple connected to a precision potentiometer and a mirror galvanometer from Tinsley and Co. Ltd. The e.m.f. could be read with an accuracy of ± 0.0005 mv. The couple was mounted in an alumina tube having two bores, the tube being sealed with fused alumina cement at one end. As the melting point of alumina is considerably higher than that of platinum this sealing of the end had to be done with considerable care. The more commonly used external thermocouple sheath would, however, considerably reduce the rate of heat transfer from the surroundings to the hot junction, and hence make the temperature measurements less reliable than the present ones. The thermocouple was standardized by determining the e.m.f.'s at the melting point of aluminum and silver, and plotting the deviations from the standard reference table of Bureau of Standards Research Paper 530.⁹ The furnace was of the ordinary electrically heated vertical type. The nickel-chromium heating wire was wound on a "Pythagoras" (Trade Mark, Porzellan-Manufaktur, W. Haldenwanger, Berlin, Germany) tube and covered with alundum cement. The space between the heating element and the outside wall was filled with silogel powder. The windings were bifilar, and more closely spaced toward the ends of the furnace, to compensate for the extra loss of heat there. A voltage stabilizer was used for the heating current. The furnace tube was internally heat insulated toward the bottom with a porous magnesia firebrick and toward the top by a similar, but more porous firebrick with appropriate holes for the thermocouple, a seeding tube and a mechanical device for stirring the melt. The poorer heat insulation of the top firebrick around the thermocouple caused the first

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