

Phase Diagrams of the Binary Systems of Some Metal β -Diketonates¹⁾

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Synopsis. Phase diagrams of the binary systems consisting of some unchanged β -diketone chelates were determined. A combination of the chelate compounds which had the same coordination structures gave a mixed crystal system, and that of different coordination structures gave a eutectic system.

Separation of an impurity from a matrix compound by zone refining is governed by their solid-liquid phase diagram. A great number of phase diagrams have been determined on metals and inorganic and organic substances. However, those of metal chelate compounds are little known, and this is, in part, due to their thermal instabilities such as decomposition prior to melting.

We have prepared a certain range of metal 1,5-dialkylpentane-2,4-dionates which are stable enough in molten state without any decomposition, in connection with their application to zone refining.

This note is to report on the solid-liquid phase diagrams of binary mixtures consisting of such chelate compounds with common ligands.

Experimental

Materials. All the chelates were reported previously,^{2,3)} except Zr(DNPM)₄ and Hf(DNPM)₄, where DNPM stands for a dipropionylmethanate anion. The last two chelates were prepared by an addition of aqueous sodium carbonate into a water-methanol mixture containing the β -diketone ligand and a metal oxychloride (4 : 1 mole ratio of a ligand to a metal ion) until pH 6. Yellow tinged white precipitate was collected by filtration, then recrystallized from aqueous methanol to yield white needles. mp 59.0—60.0 °C, Found: C, 55.59; H, 7.24%. Calcd for C₂₈H₄₄O₈Zr: C, 56.09; H, 7.34%, λ_{\max} in cyclohexane 272 nm, log ϵ_{\max} 4.53. mp 54.0—55.0 °C, Found: C, 48.61; H, 6.61%. Calcd for C₂₈H₄₄O₈Hf: C, 48.96; H, 6.41%, λ_{\max} in cyclohexane 272 nm, log ϵ_{\max} 4.57.

Measurements. Temperatures of phase transitions were determined by differential thermal analysis method^{4,5)} with 3—6 mg of chelate samples of various compositions on a Rigakudenki Thermoflex 8001, α -alumina powder being used as a reference material. The heating rates were kept constant in the region of 10—15 °C/min. Electronic spectra were measured at room temperature with a Hitachi 124 double beam spectrophotometer in appropriate solvents.

Results and Discussion

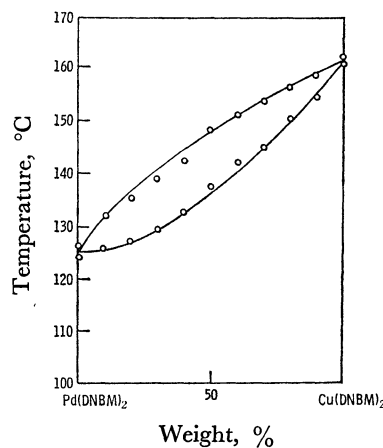
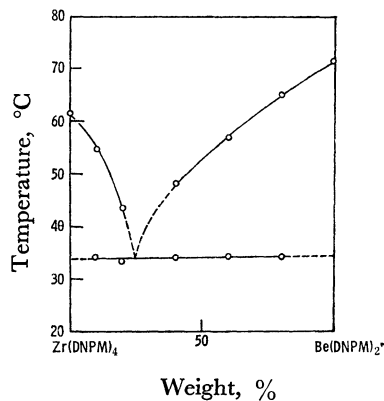
A Pd(DNBM)₂—Cu(DNBM)₂ system forms mixed crystal over the entire range of compositions, as shown in Fig. 1. Binary systems which form mixed crystals are summarized in Table 1.

Figure 2 shows the eutectic phase diagram of a Zr(DNPM)₄—Be(DNPM)₂ system. Some other eutectic system are listed in Table 2.

TABLE 1. BINARY SYSTEMS FOR MIXED CRYSTAL

Compound ^{a)}	mp(°C)	Compound ^{a)}	mp(°C)	Coord. Structure
Al(AA) ₃	191	Cr(AA) ₃	217	O _h —O _h ^{b)}
Rh(AA) ₃	260	Cr(AA) ₃	217	O _h —O _h ^{b)}
Zr(DNPM) ₄	60	Hf(DNPM) ₄	55	c)
Pd(DNBM) ₂	134	Cu(DNBM) ₂	161	D _{4h} —D _{4h}
Pd(DIVM) ₂	136	Cu(DIVM) ₂	162	D _{4h} —D _{4h}
Fe(DIVM) ₃	51	Co(DIVM) ₃	53	O _h —O _h

a) AA and DIVM stand for acetylacetonate and diisovalerylmethanate anions, respectively. b) Ref. 5. c) Archimedean antiprism—Archimedean antiprism.

Fig. 1. Phase diagram of the binary system Pd(DNBM)₂—Cu(DNBM)₂, where DNBM stands for a dibutyrylmethanate anion.Fig. 2. Phase diagram of the binary system Zr(DNPM)₄—Be(DNPM)₂.

Absorption maxima of the π - π , d-d and d- π transitions in the present 1,5-dialkylpentane-2,4-dionates are essentially superimposable to those of the acetylacetonates with the same metal ions, respectively, though a

TABLE 2. BINARY SYSTEMS FOR EUTECTIC

Compound(A)	mp(°C)	Compound(B)	mp(°C)	Eutectic Point		Coord. Structure
				mp(°C)	A%	
Be(AA) ₂	110	Cr(AA) ₃	217	98	83	T _d -O _h
Be(AA) ₂	110	Al(AA) ₃	195	97	72	T _d -O _h
Zr(DNPM) ₄	60	Be(DNPM) ₂	70	33	74	a
Zr(DNPM) ₄	60	Co(DNPM) ₃	53	32	60	b
Fe(DIVM) ₃	51	Cu(DIVM) ₂	162	49	98	O _h -D _{4h}
Fe(DIVM) ₃	51	Pd(DIVM) ₂	136	48	ca. 99	O _h -D _{4h}
Be(DIVM) ₂	50	Pd(DIVM) ₂	136	50	ca. 100	T _d -D _{4h}
Be(DIVM) ₂	50	Cu(DIVM) ₂	162	32	ca. 100	T _d -D _{4h}

a) Archimedean antiprism-T_d. b) Archimedean antiprism-O_h.

TABLE 3. COORDINATION AND CRYSTAL STRUCTURES OF ACETYLACETONATES

Compound	Coord. Structure	Crystal Structure					Reference
		a	b	c	β	Space Group	
Co(AA) ₃	O _h	14.16	7.48	16.43	98	P2 ₁ /c	7
Al(AA) ₃	O _h	14.25	7.68	16.17	99	P2 ₁ /c	8
Rh(AA) ₃	O _h	13.94	7.51	16.43	98	P2 ₁ /c	9
Cr(AA) ₃	O _h	14.03	7.55	16.38	99	P2 ₁ /c	8, 10
Fe(AA) ₃	O _h	15.47	13.58	16.57		Pbca	11
Cu(AA) ₂	D _{4h}	11.24	4.68	10.24	92	P2 ₁ /n	12
Pd(AA) ₂	D _{4h}	10.79	5.19	10.16	92	P2 ₁ /n	13
Be(AA) ₂	T _d	13.49	11.32	7.76	100	P2 ₁	14
Zr(AA) ₄	a)	19.80	8.35	14.10	102	P2/c	15
Hf(AA) ₄	a)						16

a) Archimedean antiprism.

few of them showing a slight increase in the ligand field due to the electronic effect of alkylsubstituents.⁶⁾ It is obvious, therefore, that the 1,5-dialkylpentane-2,4-dionates have the same coordination structures with those of the corresponding acetylacetonates. Coordination structures of the acetylacetonates are well known as listed in Table 3, as well as their crystal structures. The crystal structures therein seem to correlate with the coordination structures of the central metal ions, if the ligand is acetylacetonate anion in common.

Coordination structures of the present chelate compounds listed in Tables 1 and 2 are those presumed on the basis of the above presumption, except those of the acetylacetonates. One can readily notice that the combinations of chelates which form mixed crystals have the same coordination structures, and those forming eutectic have different ones.

In general, component substances of similar molecular structures afford a mixed crystal system of a substitution form. In the metal chelate compounds with a common ligand anion, the structural similarity requires not only the same coordination structure but also similar sizes of the central metal ions. Difference in ionic radii, 0.6 Å, between palladium(II) and copper(II) would be the largest among those of the combinations of metal ions which form metal chelates of the same coordination structures, and the chelates of these metal ions are still capable of forming a binary mixed crystal.

References

- 1) Contribution No. 333 from the Department of Organic Synthesis, Kyushu University.
- 2) I. Yoshida, H. Kobayashi, and K. Ueno, *J. Inorg. Nucl. Chem.*, **35**, 4061 (1973).
- 3) I. Yoshida, H. Kobayashi, and K. Ueno, *This Bulletin*, **47**, 2203 (1974).
- 4) M. J. Visser and W. H. Wallace, *Du Pont Thermogram*, **3**, 9 (1966).
- 5) H. Kaneko, H. Kobayashi, and K. Ueno, *Talanta*, **14**, 1403 (1967).
- 6) I. Yoshida, H. Kobayashi, and K. Ueno, *This Bulletin*, **45**, 2768 (1972).
- 7) V. M. Padmanabham, *Proc. Indian Acad. Sci.*, **47A**, 329 (1958). *Chem. Abstr.*, **52**, 17881h (1958).
- 8) E. A. Shugam and L. M. Shkolnikova, *Kristallografiya*, **1**, 478 (1956). *Chem. Abstr.*, **52**, 9708c (1958).
- 9) E. B. Parker and J. C. Morrow, *Acta Crystallogr.*, **21**, A147 (1966).
- 10) B. Morosin, *ibid.*, **19**, 131 (1965).
- 11) R. B. Roof, Jr., *ibid.*, **9**, 781 (1956).
- 12) E. G. Cox and K. C. Webster, *J. Chem. Soc.*, **1935**, 731.
- 13) E. A. Shugam, L. M. Shkolnikova, and V. V. Zelentsov, *Zh. Strukt. Khim.*, **7**, 128 (1966). *Chem. Abstr.*, **64**, 18555e (1966).
- 14) V. Amirthalingam, V. M. Padmanabham, and J. Shankar, *Acta Crystallogr.*, **13**, 201 (1960).
- 15) D. Grdenić and B. Matković, *ibid.*, **12**, 817 (1959).
- 16) E. M. Larsen, G. Terry, and J. Leddy, *J. Amer. Chem. Soc.*, **75**, 5107 (1953).