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Stability trends of some 1:1 and 2:1 malonato and 1,1-cyclobutanedicarboxylato cobalt, nickel, copper and zinc chelates*

In the course of investigation of the stability of metal chelate species formed with the anion of 1,1-cyclobutanedicarboxylic acid (a ligand analogous to the malonate anion), determination of the stoichiometric formation constants of 1:1 and 1:2 metal chelate species of the 3d transition metals (cobalt, nickel, copper and zinc) involving both CBDA and malonate anions was undertaken at 25° and $I = 0.1$ (KNO_3). With malonate K_1 values, the results were in fair agreement with results of others^{1,2}; and with CBDA anion, behavior was sufficiently different from that of malonate to warrant comment.

The method used in this work has been described previously³; thus, it need not be redescribed. The results are compared (Table I) with results of YASADA *et al.*² (in parenthesis).

TABLE I

STEP FORMATION CONSTANTS OF 1:1 AND 1:2 CHELATE SPECIES (AT 25°; $I = 0.1$)

Metal (II) ion	Malonato species		CBDA species	
	K_1	K_2	K_1	K_2
Co	$9.0 \pm 0.1 \times 10^2$	30 ± 3	$1.6 \pm 0.2 \times 10^2$	10 ± 5
Ni	$1.88 \pm 0.02 \times 10^3$ (1.6×10^3)	47 ± 3	$2.2 \pm 0.2 \times 10^2$	10 ± 5
Cu	$1.04 \pm 0.01 \times 10^5$ (1×10^5)	840 ± 10	$1.03 \pm 0.01 \times 10^5$	1300 ± 100
Zn	$9.3 \pm 0.1 \times 10^2$ (5×10^2)	30 ± 5	$3.4 \pm 0.1 \times 10^2$	30 ± 10

Considering the relatively high ionic strength (0.1) in our experiments, it would be invalid to compute and report thermodynamic stability constants for comparison with other data at $I \rightarrow 0$. A glance at the variety of miscellaneous malonate chelate stability data compiled by SILLÉN AND MARTELL⁴ reveals recorded values of $\log^T K_1(\text{Cu})$ ranging from 5.60 to 5.80, as well as other uncertainties, and the fact that K_2 values in metal malonate systems generally have not been reported. However, in the case of copper malonate at 20°, $I = 0.1$ (KNO_3), GELLES AND NANCOLLAS¹ reported $K_1 = 0.65 \times 10^5$ and $\beta_2 = 5.4 \times 10^7$, yielding $K_2 = 8.3 \times 10^2$ in excellent agreement with our 8.4×10^2 . Their value for K_1 , however, is substantially lower than ours (1.04×10^5), as well as that of YASADA *et al.*².

It is noteworthy that, although 1:1 malonate and CBDA chelates of copper (II) are nearly identical in stability, both the 1:1 and 1:2 CBDA chelates formed in the cases of cobalt, nickel and zinc are much less stable than corresponding malonate species. In changing the ligand from malonate to the analogous, but more constrained, CBDA entity, a reversal in stability of 1:1 nickel and zinc chelate species occurs.

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With malonate the order of affinity of cation for ligand is $\text{Cu} \gg \text{Ni} > \text{Zn} \cong \text{Co}$; with CBDA the observed order is $\text{Cu} \gg \text{Zn} > \text{Ni} > \text{Co}$.

From the relative magnitudes of β_2 values it is apparent that CBDA buffer solutions would be highly effective eluants in cation-exchange elution separations of copper and nickel. In view of the nearly identical affinities of Cu(II) and Ni(II) for Dowex 50-X8 cation-exchange resin, for example, elution of copper and nickel with ammonium CBDA should afford a separation factor as large as 6×10^4 . Indeed, it has been possible in this laboratory to achieve quantitative recovery of copper from nickel or zinc by selective elution of from 0.1 to 2.0 mmoles of Cu(II) from 2 mmoles of binary mixture on 40-50 mesh Dowex 50-X8 resin beds, 2 mm in diameter and 60 mm long, using 60-100 ml of 0.1 M $(\text{NH}_4)_{1.5}\text{H}_{0.5}$ CBDA (followed by 300 ml of distilled water) at 5 ml/min.

*Institute for Atomic Research and
Department of Chemistry,
Iowa State University,
Ames, Iowa 50010 (U.S.A.)*

J. E. POWELL
D. K. JOHNSON

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