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Potentiomeric and Polarographic Studies on Complex Formation of Cadmium(II) Ion with Ethylenediaminemonoacetic Acid

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The complex formation equilibria between Cd(II) ion and ethylenediaminemonoacetic acid (EDMA) were examined by potentiometry in a 1.0 mol dm^{-3} NaClO$_4$ solution at (25.00±0.02) °C, and it was found that neither protonated nor hydrolyzed complex was formed in the range of pH from 2 to 10. The formation constants of Cd(II)–EDMA complexes as well as the protonation constants of EDMA anion determined were as follows: log $\beta_{101}=6.86$, log $\beta_{102}=12.32$; log $\beta_{011}=9.97$, log $\beta_{021}=16.71$, log $\beta_{031}=18.76$, where $\beta_{pqr}=[\mathrm{M}_p\mathrm{H}_q\mathrm{L}_r]/[\mathrm{M}]^p[\mathrm{H}]^q[\mathrm{L}]^r$. The formation constants were also examined polarographically.

In the previous works[1,2] we examined the complex formation equilibria of Cd(II) ion with *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetate (L=hedta^{3-}) and ethylendiamine-*N*,*N*,*N'*,*N'*-tetraacetate (L=edta^{4-}) by potentiometric titrations over a wide range of pH, and found that a number of protonated complexes of the type MH$_q$L ($q=1$, 2 for the HEDTA complex and $q=1$, 2, 3 for the EDTA complex) are formed in the acidic region (pH<*ca.* 3.5). Furthermore, from comparison of the successive protonation constants of the complexes with those of the corresponding ligands, we derived the conclusion that the protons of the protonated complexes are located at the acetate groups of the ligands. It can be deduced therefrom that the chelate formation between Cd(II) ion and the ligands occurs through the two nitrogen atoms and at least one acetate group of the ligands and thus when all the acetate groups of the ligands are protonated, such ligands do not form any complex with Cd(II) ion. Then, a question may arise: if the ethylenediamine skeleton has only one acetate group, does such a ligand form a protonated complex with Cd(II) ion ? The present work thus aims at examining the possibility of the formation of protonated complexes between Cd(II) and ethylenediaminemonoacetate (L=edma$^-$) ions. Although the complex formation of Cd(II) ion with edma$^-$ anion was already studied by Fujii *et al.*[3] by polarography, their measurements were done only in a neutral solution (pH 6.0—7.0) of ionic strength of 0.2 mol dm^{-3}. Thus, in the present work we shall reexamine the equilibria between Cd(II) and edma$^-$ ions by potentiometric titrations over a wide range of pH, especially noting the acidic region, in which protonated complexes might be formed. Furthermore, for comparison, we shall describe the results of polarographic measurements performed under the same experimental conditions as for the potentiometric titrations.

Symbols

h	Concentration of hydrogen ion at equilibrium
m	Concentration of metal ion at equilibrium
H	Analytical excess of hydrogen ion in a test solution
c_{Cd}	Total concentration of Cd(II)
L	Ethylenediaminemonoacetate anion (edma$^-$)
c_{L}	Total concentration of L
l	Concentration of free L
X	Degree of neutralization of HL: $(-H+h-K_{\mathrm{w}}/h)/c_{\mathrm{L}}$
K_{w}	Autoprotolysis constant of water in 1 mol dm^{-3} NaClO$_4$ solution ($10^{-13.95}$ mol^2 dm^{-6}).[4]
$\bar{n}$	Average number of protons bound to one L
$\bar{Z}$	Average number of edma anions bound to one Cd(II)
p	Number of cadmium ions bound to complex species
q	Number of protons bound to complex species
r	Number of edma anions bound to complex species
s	Number of chloride anions bound to complex species
β_{pqrs}	Equilibrium constant for the reaction $p\mathrm{Cd} + q\mathrm{H} + r\mathrm{L} + s\mathrm{Cl} = \mathrm{Cd}_p\mathrm{H}_q\mathrm{L}_r\mathrm{Cl}_s$
[ ]	Concentration
$[\ ]_t$	Total concentration
D_{Cd}	Diffusion coefficient of aqua cadmium(II) ion
D_{c}	Average diffusion coefficient of Cd(II)–EDMA complexes
$(E^{r}{}_{1/2})_{\mathrm{Cd}}$	Reversible half-wave potential of aqua Cd(II) ion
$(E_{1/2})_{\mathrm{rev}}$	Reversible half-wave potential of the Cd(II)–EDMA system

All ionic charges are omitted for the sake of convenience.

Experimental

Reagents. *Ethylenediaminemonoacetic acid bis(hydrogen chloride) dihydrate* (Hedma·2HCl·2H$_2$O) was prepared and purified by the method described by Fujii *et al.*[5] Though we first attempted to obtain crystals of diperchlorate of ethylenediaminemonoacetic acid (EDMA), it was not successful because of their large solubility. The replacement of chloride ions of Hedma·2HCl with perchlorate ions was not attempted, because the stock solution of the ligand may not be accurately standardized with any standard metal solution and the replacement procedure may introduce impurities. Thus, the EDMA solutions used in the present work necessarily contained chloride ions exactly twice as much as edma$^-$ anions. The result of the elemental analysis of the EDMA crystals obtained was as follows: Calcd for C$_4$H$_{10}$N$_2$O$_2$·2HCl·2H$_2$O: C, 21.26; H, 7.10; N, 12.34%. Found: C, 21.65; H, 7.12; N, 12.29%.

All other chemicals were prepared and purified by the methods described previously.[1,2]

Potentiometric Measurements. The apparatus and the experimental procedures used for potentiometric titrations have been described in the previous paper.[1] The measurements were carried out in a paraffin oil thermostat at (25.00±0.02) °C by using glass and cadmium-amalgam electrodes. Sodium perchlorate was used as an indifferent salt to keep the perchlorate concentration at 1.0 mol dm^{-3} in all runs.

Polarographic Measurements. The polarographic appratus and the experimental procedures have been described previously.[6]

Results and Discussion

Evaluation of Protonation Constants of EDMA. Overall protonation constants of the edma base, β_{0n1}, were determined from the formation function, $\bar{n}$ and $\bar{n}_{\mathrm{cacld}}$, by using the generalized least squares method;[1]

$$\bar{n}_{\mathrm{calcd}} = \left(\sum_{n=1}^{3} n\beta_{0n1}h^n\right)\Big/\left(1+\sum_{n=1}^{3}\beta_{0n1}h^n\right), \qquad (1)$$

$$\bar{n} = \frac{c_{\mathrm{L}}+H-h+(K_{\mathrm{w}}/h)}{c_{\mathrm{L}}}. \qquad (2)$$

The protonation constants obtained were $\log\beta_{011}=9.97$, $\log\beta_{021}=16.71$, and $\log\beta_{031}=18.76$. Fujii *et al.*[7] reported the values of $\log\beta_{011}=10.15$, $\log\beta_{021}=16.80$, and $\log\beta_{031}=18.95$ at an ionic strength 0.2 at 25.0 °C.

Determination of the Composition and the Formation Constants of Complexes by Potentiometric Titrations. Titration curves of the Cd(II)-EDMA solution were shown in Fig. 1. The experiments were carried out under the conditions that the ratios of $c_{\mathrm{Cd}}/c_{\mathrm{L}}$ were 1/1, 1/2, and 1/5, where c_{Cd} and c_{L} were changed from 1 mmol dm^{-3} to 5 mmol dm^{-3} and from 5 mmol dm^{-3} to 25 mmol dm^{-3}, respectively. For each run, c_{Cd} and c_{L} were kept practically constant. As can be seen in Fig. 1, the values of X were independent of c_{Cd} and c_{L} over the pH range 2—5. This result showed that no proton was released from the ligand by the complex formation.

Since a stock solution of the ligand EDMA contains chloride ions, the equilibria of the Cd(II)–EDMA system may be described by the general formula including chloride ions;

$$p\mathrm{Cd}^{2+} + q\mathrm{H}^+ + r\mathrm{L}^- + s\mathrm{Cl}^- = \mathrm{Cd}_p\mathrm{H}_q\mathrm{L}_r\mathrm{Cl}_s{}^{(2p+q-r-s)}, \qquad (3)$$

with the equilibrium constant, β_{pqrs}. From the material balance for Cd(II) ion, we obtain

$$\begin{aligned} c_{\mathrm{Cd}} &= [\mathrm{Cd}] + \sum_p\sum_q\sum_r\sum_s p[\mathrm{Cd}_p\mathrm{H}_q\mathrm{L}_r\mathrm{Cl}_s] \\ &= m + \sum_p\sum_q\sum_r\sum_s p\beta_{pqrs}m^p h^q l^r[\mathrm{Cl}]^s. \qquad (4) \end{aligned}$$

Rearrangement of Eq. 4 leads to

$$\begin{aligned} \xi &= \log\{(c_{\mathrm{Cd}}-m)/m\} \\ &= \log\{\sum_p\sum_q\sum_r\sum_s p\beta_{pqrs}m^{p-1}h^q l^r[\mathrm{Cl}]^s\}. \qquad (5) \end{aligned}$$

As a first approach for analyzing data, we assume that only one complex is formed; then Eq. 5 is reduced to

$$\begin{aligned} \xi = \log p\beta_{pqrs} &+ (p-1)\log m + q\log h \\ &+ r\log l + s\log[\mathrm{Cl}]. \qquad (6) \end{aligned}$$

The plots of ξ *vs.* $-\log h$ are shown in Fig. 2. From this figure, we can see the following facts in the pH range 2—5. (1) Although ξ seemed to depend on c_{L}, it was independent of $-\log h$, and therefore, ξ can not be a

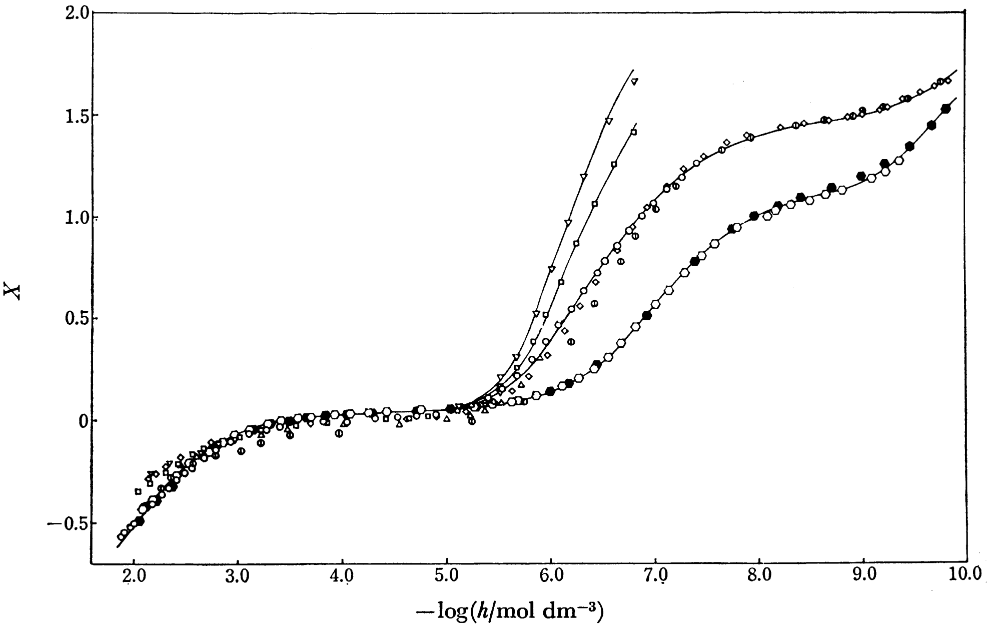

Fig. 1. Degree of neutralization, X, of ethylenediaminemonoacetic acid (EDMA) solutions for the Cd(II)-EDMA systems.

(○): $c_{\mathrm{Cd}}=0.0$ mol dm^{-3}, $c_{\mathrm{L}}=0.005013$ mol dm^{-3};
(●): $c_{\mathrm{Cd}}=0.0$ mol dm^{-3}, $c_{\mathrm{L}}=0.01003$ mol dm^{-3};
(⦶): $c_{\mathrm{Cd}}=0.001016$ mol dm^{-3}, $c_{\mathrm{L}}=0.005018$ mol dm^{-3};
(△): $c_{\mathrm{Cd}}=0.002611$ mol dm^{-3}, $c_{\mathrm{L}}=0.005057$ mol dm^{-3};
(◇): $c_{\mathrm{Cd}}=0.002650$ mol dm^{-3}, $c_{\mathrm{L}}=0.01263$ mol dm^{-3};
(▽): $c_{\mathrm{Cd}}=0.005074$ mol dm^{-3}, $c_{\mathrm{L}}=0.005183$ mol dm^{-3};
(□): $c_{\mathrm{Cd}}=0.005045$ mol dm^{-3}, $c_{\mathrm{L}}=0.01007$ mol dm^{-3};
(○): $c_{\mathrm{Cd}}=0.005055$ mol dm^{-3}, $c_{\mathrm{L}}=0.02514$ mol dm^{-3}.

Solid lines are the values of X calculated by the use of the formation constants in Table 1.

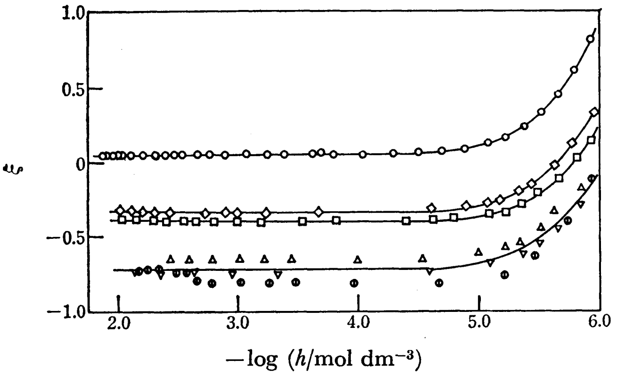

Fig. 2. Relationships between ξ and $-\log h$. Symbols are the same as those in Fig. 1. Solid lines are the values calculated by the use of the formation constants in Table 1 and of the formation constant of the $CdCl^+$ complex, $10^{1.35}$.

function of l, which may be approximately calculated by the following equation:

$$l \simeq c_L/\sum_{n=1}^{3}\beta_{0n10}h^n. \tag{7}$$

(2) The dependence of ξ on c_L should be explained in terms of the contribution of chloride ions, instead of EDMA anion, in the complex formation. The concentration of chloride ion was $2c_L$ in the present experiment. (3) ξ was independent of c_{Cd} at constant c_L (0.005 mol dm^{-3}) within experimental errors. From these results, we can conclude that no Cd–edma complex but a mononuclear $CdCl_s^{(2-s)+}$ complex formed in the pH range of 2—5.

Since $c_{Cd} < c_{Cl}$ in all cases and the degree of complexation of Cd(II) ion with chloride ion is rather small, we can assume that the concentration of free chloride ion ($[Cl]_f$) is almost equal to that of total chloride ion ($[Cl]_t$). When ξ is plotted against log $[Cl]_t$ calculated as $\log(2\times c_L)$, a linear relation of the unit slope resulted (see Fig. 3). Thus, the complex formation, $Cd^{2+}+Cl^- = CdCl^+$, ($p=1$, $q=0$, $r=0$, and $s=1$), took place, and the formation constant was determined as $\log\beta_{1001}=1.35$ by application of a successive approximation to Eq. 6. The constant coincides with the value of 1.35 reported by Vanderzee and Dawson in a 1 mol dm^{-3} $NaClO_4$ solution at 25 °C.[8]

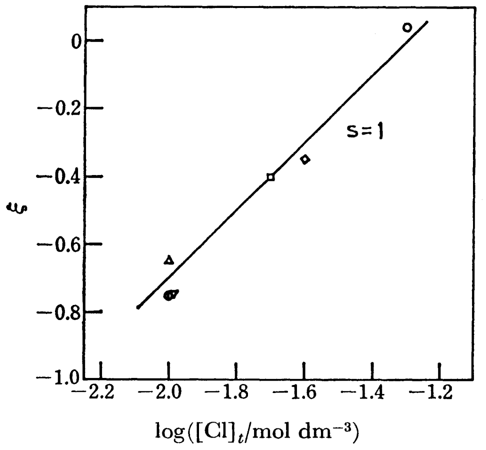

Fig. 3. Plot of ξ against log $[Cl]_t$ at $-\log(h/\text{mol dm}^{-3})=2.4$. $[Cl]_t$ denotes the total concentration of choride ion.

Above pH 5.5, the titration curves of solutions containing Cd(II) ions deviated from that of the solution containing only the ligand, as shown in Fig. 1. In the cases of $c_{Cd}/c_L=1/1$ and $1/2$, white precipitates were separated out in an alkaline region and stable emf's could not be recorded. On the other hand, the titration curves for the case of $c_{Cd}/c_L=1/5$ converged on a single curve over the pH range 5.5—10.0. Since the titration curves at $c_{Cd}/c_L=1/5$ were independent of the total concentration of Cd(II) ion (0.001—0.005 mol dm^{-3}), it is seen that no polynuclear complex species was formed. Then, the concentration of free edma is expressed as follows:

$$l = \{c_L+H-h+(K_w/h)\}/(\sum_{n=1}^{3}n\beta_{0n10}h^n), \tag{8}$$

and the formation function $\bar{Z}$ is expressed by

$$\bar{Z} = (c_L-\sum_{n=1}^{3}\beta_{0n10}lh^n)/c_{Cd} \quad (\beta_{0010}=1), \tag{9}$$

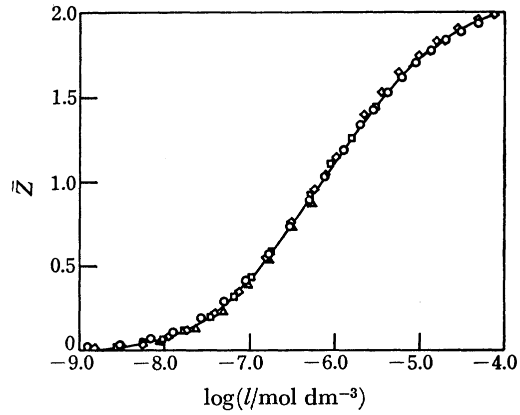

Fig. 4. Relationships between the formation function $\bar{Z}$ and log l. Solid line is the best fit curve calculated by Eq. 11. Symbols are the same as those in Fig. 1.

where c_{Cd} is the total concentration of Cd(II) ion. Figure 4 demonstrates the plots of $\bar{Z}$ *vs.* log l. As can be seen in this figure, a single curve was obtained regardless of the variations of c_{Cd}, c_L, and $[Cl]_t$. Therefore, no mixed complexes of Cd(II) ion with chloride and edma$^-$ ions were formed. Furthermore, the values of $\bar{Z}$ approached 2.0 as the values of log l increased. The formation curve thus obtained could be overlapped with a normalized curve

$$\bar{Z}_{\text{calcd}} = (pv+2v^2)/(1+pv+v^2), \tag{10}$$

with $p=\beta_{1010}/\sqrt{\beta_{1020}}$, and $\log v=\log l+1/2\,\log\beta_{1020}$,[9] and thus the formation of the CdL^+ and $CdL_2{}^0$ complexes was concluded. The formation constants of these complexes were evaluated from the best fit curve with the experimental one. By using the values, $\log\beta_{1010}=6.9$ and $\log\beta_{1020}=12.3$, thus determined as the initial values, the formation constants were refined by means of a generalized least squares method in which the minimum error square sum $U=\Sigma(\bar{Z}_{\text{calcd}}-\bar{Z})^2$ was

TABLE 1. FORMATION CONSTANTS OF Cd(II)–EDMA COMPLEXES (log β_{pqrs}) IN 1.0 mol dm^{-3} NaClO$_4$ SOLUTION AT 25.0 °C

$\beta_{pqrs}=[\mathrm{M}_p\mathrm{H}_q\mathrm{L}_r\mathrm{Cl}_s{}^{(2p+q-r-s)+}]/[\mathrm{M}^{2+}]^p[\mathrm{H}^+]^q[\mathrm{L}^-]^r[\mathrm{Cl}^-]^s$
log $\beta_{0110}=9.97\pm0.02$, log $\beta_{0210}=16.71\pm0.02$,
log $\beta_{0310}=18.76\pm0.02$.

	log β_{1010}	log β_{1020}
Potentiometry	6.86±0.02	12.32±0.02
Polarography	7.20±0.05	13.13±0.05
	(8.48)	(13.23)

( ): Ref. 3.

searched, where $\bar{Z}_{\mathrm{cacld}}$ is given by

$$\bar{Z}_{\mathrm{calcd}} = (\beta_{1010}l+2\beta_{1020}l^2)/(1+\beta_{1010}l+\beta_{1020}l^2). \qquad (11)$$

The results were shown in Table 1. The solid curve in Fig. 4 represents the calculated one by using the final values.

Determination of the Formation Constants by Polarography. As described in the section of potentiometric measurements, the CdL$^+$ and CdL$_2$ complexes were formed at pH>6.0. In order to examine the polarographic behavior of these complexes, the change of the half-wave potential with l was measured over the pH range 6.0—7.5. No buffer reagent was used, because the test solutions have a sufficient buffer capacity due to the ligand itself which is present in a large excess in comparison with Cd(II) ion. Single waves with the diffusion-controlled limiting current were observed and the conventional log-plots of the current-potential curves yielded straight lines with the reciprocal slopes of (30±1) mV, in accord with the fact that the reversible two-electron reduction occurred. Since the half-wave potential shifted to the negative side with the increase of pH, the formation constants of the complexes can be determined from this shift by the method developed by DeFord and Hume.[10,11]

DeFord and Hume's function F_0 is defined as follows:

$$F_0 = \sum_{r=0}^{N}\beta_{10r0}l^r$$
$$= (D_{\mathrm{Cd}}/D_{\mathrm{c}})^{1/2}\exp\left(\frac{nF}{RT}\right)\{(E^r_{1/2})_{\mathrm{Cd}}-(E_{1/2})_{\mathrm{rev}}\}. \qquad (12)$$

The factor $(D_{\mathrm{Cd}}/D_{\mathrm{c}})^{1/2}$ was obtained from the ratio of the diffusion current of Cd(II) ion to that of the complexes. The measured value of −0.575 V *vs.* SCE was used for $(E^r_{1/2})_{\mathrm{Cd}}$. A new function $F_1=(F_0-1)/l$ is defined and extrapolation of the F_1 curve toward $l=0$ gives an intercept corresponding to β_{1010}. The procedure was repeated until a horizontal line was obtained. The sets of the plots analyzed to obtain β_{10r0} are shown in Fig. 5. The formation constants β_{1010} and β_{1020} thus found are given in Table 1. In these procedures, the complex formation of Cd(II) ion or Cd–edma complex with chloride ion was neglected.

As can be seen from Table 1, the values of the formation constants of 1 : 1 and 1 : 2 Cd(II)–edma complexes obtained by polarography were larger than the values obtained by potentiometry. Such discrepancies have sometimes been observed for the complex formation of Cd(II) ion with other multidentate ligands. The value of log β_2 of the Cd(II)–diethylenetriamine complex obtained by potentiometry[12,13] is 13.9, whereas the value determined by polarography[14] is 14.8. Log β_1 of the Cd(II)–triethylenetetramine complex is estimated to be 10.8 by potentiometry,[15] whereas the value for this complex obtained by polarography[14] is 13.9. Thus the values obtained by polarography are often larger than those obtained by potentiometry. The difference in these values may be attributed to the difference in the methods employed, but the reason is not clear yet.

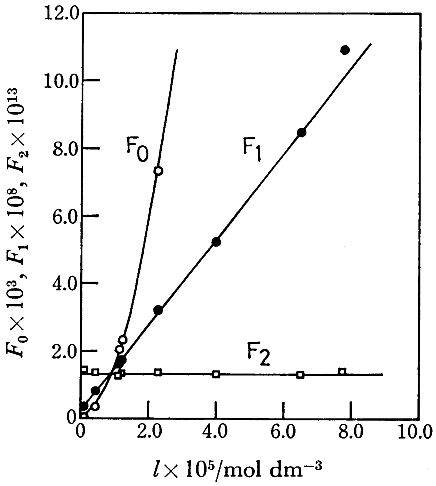

Fig. 5. Dependence of F_p (p=0, 1, 2) on l at total EDMA concn=0.0100 mol dm^{-3}.

The ethylenediaminemonoacetate ligand formed no protonated complex with Cd(II) ion. In combination with the results obtained in the previous works for the Cd(II)–edta[2] and –hedta[1] complexes, we concluded that the two nitrogen atoms and at least one acetate group are indispensable for the chelate formation of a diaminepolyacetate ligand with Cd(II) ion.

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