Supporting Information

Cadmium(II) Complex Formation with Cysteine and Penicillamine

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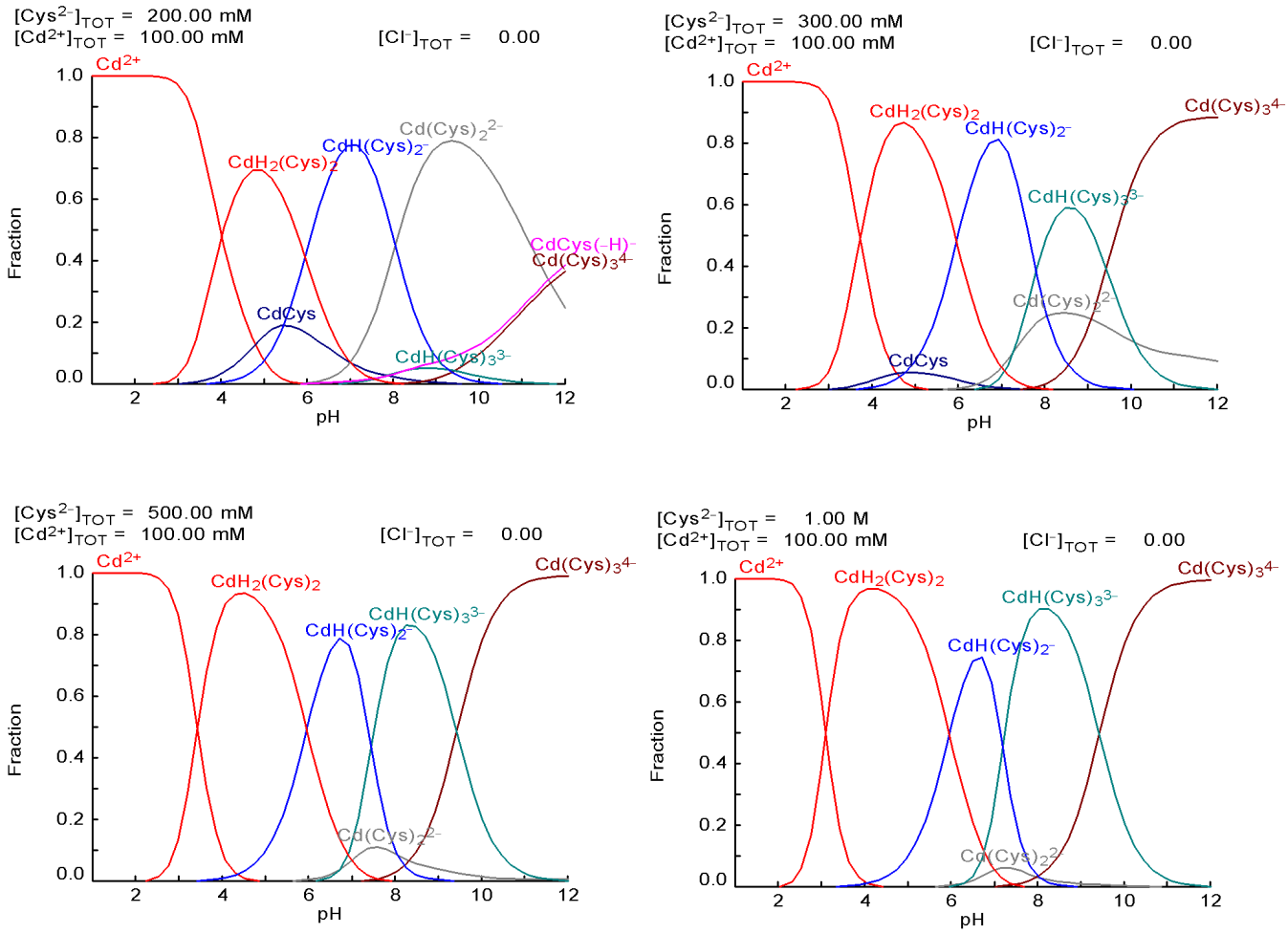

Figure S-1. Distribution diagrams for cadmium(II) cysteine complexes as a function of pH in solutions **A**, **B**, **D** and **E**, containing $C_{Cd^{2+}}$ ~ 0.1 mol dm^{-3} and (H_2Cys / Cd^{2+}) ratios 2.0, 3.0, 5.0 and 10.0 (*Ref.* 14).

The following complexes were considered as the result of reaction between Cd^{2+}, Cys^{2-} and H^+:

$$q\ Cd^{2+} + p\ Cys^{2-} + r\ H^+ \leftrightarrow Cd_q\,(Cys)_p\,H_r \qquad \beta_{q,\,p,\,r}$$

Cd(Cys) (log $\beta_{1,\,1,\,0}$ = 10.3), Cd(Cys)(OH) (log $\beta_{1,\,1,\,-1}$ = 2.42), $Cd(Cys)_2$ (log $\beta_{1,\,2,\,0}$ = 16.92), Cd(HCys)(Cys) (log $\beta_{1,\,2,\,1}$ = 24.97), $Cd(HCys)_2$ (log $\beta_{1,\,2,\,2}$ = 30.93), $Cd(Cys)_3$ (log $\beta_{1,\,3,\,0}$ = 19.78) and Cd(HCys)$(Cys)_2$ (log $\beta_{1,\,3,\,1}$ = 29.21). These formation constants were calculated for cadmium(II) and cysteine complexation at 37 ºC in the ionic medium 0.15 mol dm^{-3} NaCl, with total cysteine concentration ranging between 0.005 to 0.020 mol dm^{-3} (*Ref.* 14).

The distribution diagrams in Figure S-1 were calculated with MEDUSA computer program (http://www.kemi.kth.se/medusa/). The full input file to MEDUSA is:

```
4,  21,  6,  0   /MEDUSA, t= 25 C, p= 1

H+
Cd 2+
Cys 2-
Cl-
HCys -            ,   10.26        1  0  1  0
H2Cys             ,   18.48        2  0  1  0
H3Cys +           ,   20.52        3  0  1  0
CdCys             ,   10.3         0  1  1  0
Cd(Cys)2 2-       ,   16.92        0  1  2  0
Cd(Cys)3 4-       ,   19.78        0  1  3  0
CdH(Cys)3 3-      ,   29.21        1  1  3  0
CdCys(-H) -       ,   2.42        -1  1  1  0
CdH(Cys)2 -       ,   24.97        1  1  2  0
CdH2(Cys)2        ,   30.93        2  1  2  0
Cd(OH)2           , -20.35        -2  1  0  0
Cd(OH)3-          , -33.3         -3  1  0  0
Cd(OH)4 2-        , -47.35        -4  1  0  0
Cd2OH 3+          , -9.39         -1  2  0  0
Cd4(OH)4 4+       , -32.85        -4  4  0  0
CdCl+             ,   1.98         0  1  0  1
CdCl2             ,   2.6          0  1  0  2
CdCl3-            ,   2.4          0  1  0  3
CdClOH            , -7.404        -1  1  0  1
CdOH+             , -10.08        -1  1  0  0
OH-               , -14.0         -1  0  0  0
Cd(OH)2(am)       , -13.73        -2  1  0  0
*Cd(OH)2(cr)      , -13.65        -2  1  0  0
CdCl2(c)          ,   0.68         0  1  0  2
CdCl2:2.5H2O(c)   ,   1.94         0  1  0  2
CdO(cr)           , -13.77        -2  1  0  0
CdOHCl(c)         , -3.52         -1  1  0  1
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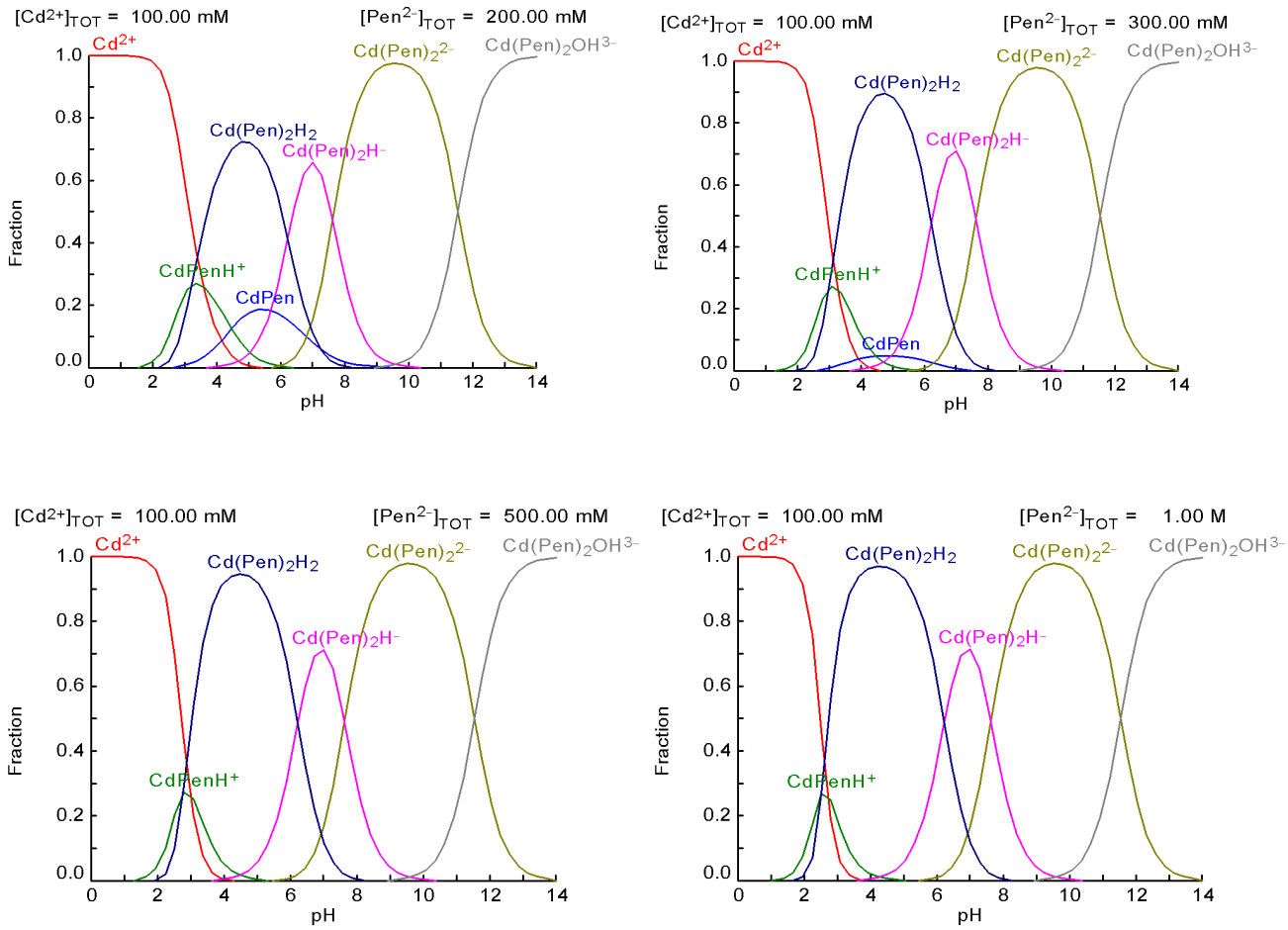

Figure S-2a. Distribution diagrams for cadmium(II) penicillamine complexes as a function of pH in solutions **H**, **I**, **K** and **L**, containing $C_{Cd^{2+}}$ ~ 0.1 mol dm^{-3} and (H_2Pen / Cd^{2+}) ratios 2.0, 3.0, 5.0 and 10.0 (*Ref.* 15). The following complexes were considered as the result of reaction between Cd^{2+}, Pen^{2-} and H^+:

$$q\ Cd^{2+} + p\ Pen^{2-} + r\ H^+ \leftrightarrow Cd_q\,(Cys)_p\,H_r \qquad\qquad \beta_{q,\,p,\,r}$$

[Cd(Pen)] (log $\beta_{1,\,1,\,0}$ = 12.68), $[Cd(HPen)]^+$ (log $\beta_{1,\,1,\,1}$ = 17.15), $[Cd(HPen)(Pen)]^-$ (log $\beta_{1,\,2,\,1}$ = 28.31), $[Cd(Pen)_2]^{2-}$ (log $\beta_{1,\,2,\,0}$ = 20.68), $[Cd(HPen)_2]$ (log $\beta_{1,\,2,\,2}$ = 34.53) and $[Cd(Pen)_2(OH)]^{3-}$ (log $\beta_{1,\,2,\,-1}$ = 9.14). These formation constants were obtained for cadmium(II) and penicillamine complexation at 25 ºC in the ionic medium 3.0 mol dm^{-3} $NaClO_4$ (*Ref.* 15).

The distribution diagrams in Figure S-2a were calculated with MEDUSA computer program (http://www.kemi.kth.se/medusa/). The full input file to MEDUSA is:

```
 3,  16,  3,  0     /HYDRA,  t=25 C
H+
Cd 2+
Pen 2-
CdPen              ,   12.68      0  1  1
CdPenH+            ,   17.15      1  1  1
Cd(Pen)2 2-        ,   20.68      0  1  2
Cd(Pen)2H -        ,   28.31      1  1  2
Cd(Pen)2H2         ,   34.53      2  1  2
Cd(Pen)2OH 3-      ,   9.14      -1  1  2
Cd(OH)2            ,  -20.35     -2  1  0
Cd(OH)3-           ,  -33.3      -3  1  0
Cd(OH)4 2-         ,  -47.35     -4  1  0
Cd2OH 3+           ,  -9.39      -1  2  0
Cd4(OH)4 4+        , -32.85      -4  4  0
CdOH+              ,  -10.08     -1  1  0
HPen -             ,   11.01      1  0  1
H2Pen              ,   19.61      2  0  1
H3Pen +            ,   22.04      3  0  1
OH-                ,  -14.0      -1  0  0
Cd(OH)2(am)        ,  -13.73     -2  1  0
Cd(OH)2(c)         ,  -13.65     -2  1  0
CdO(c)             ,  -13.77     -2  1  0
```

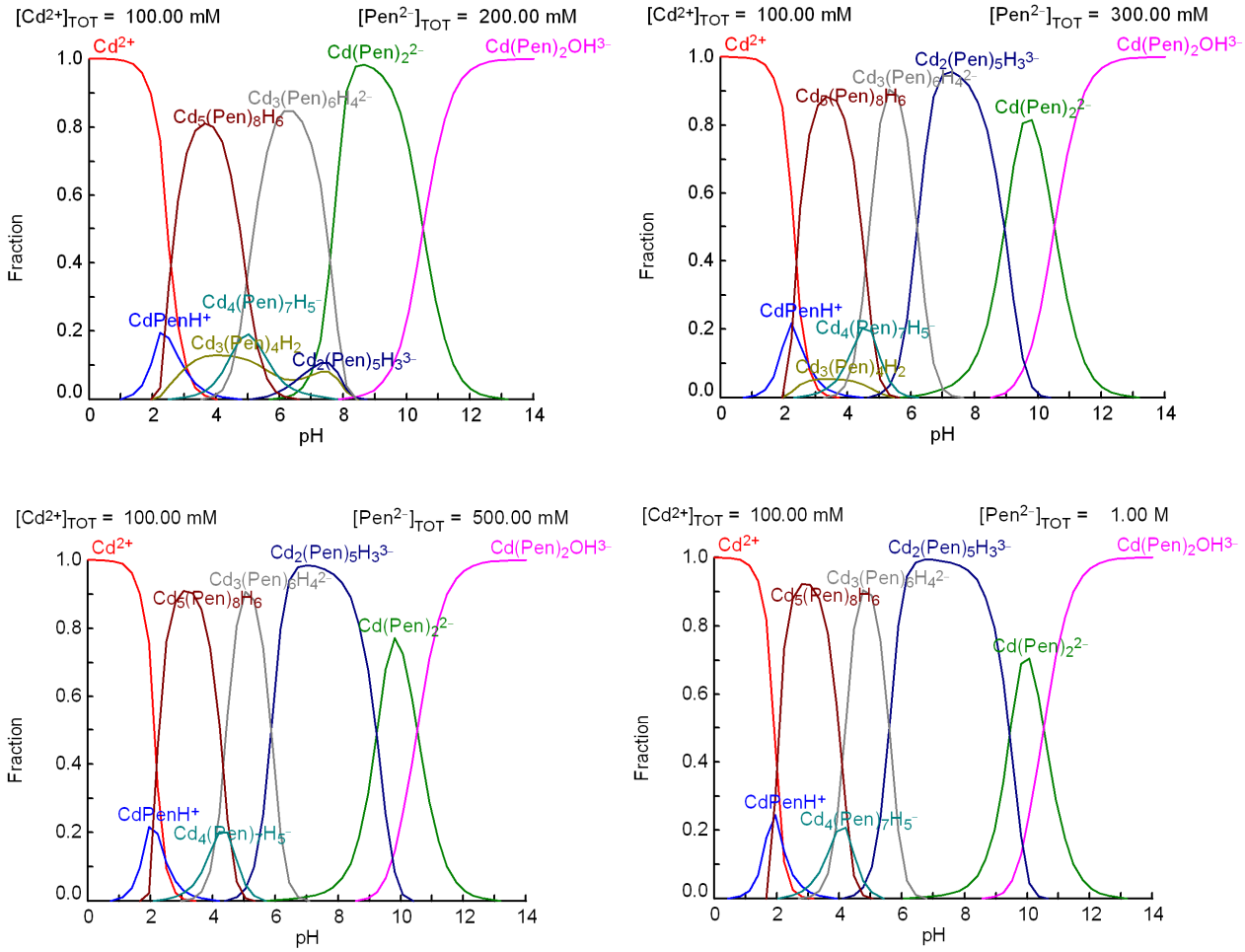

Figure S-2b. Distribution diagrams for cadmium(II) penicillamine complexes as a function of pH in solutions containing $C_{Cd^{2+}}$ ~ 0.1 mol dm^{-3} and (H_2Pen / Cd^{2+}) ratios 2.0, 3.0, 5.0 and 10.0 (*Ref.* 16). The following complexes were considered as the result of reaction between Cd^{2+}, Pen^{2-} and H^+:

$$q\ Cd^{2+} + p\ Pen^{2-} + r\ H^+ \leftrightarrow Cd_q\,(Cys)_p\,H_r \qquad\qquad \beta_{q,\,p,\,r}$$

$[Cd(HPen)]^+$ (log $\beta_{1,\,1,\,1}$ = 16.39), $[Cd(Pen)_2]^{2-}$ (log $\beta_{1,\,2,\,0}$ = 20.27), $[Cd(Pen)_2(OH)]^{3-}$ (log $\beta_{1,\,2,\,-1}$ = 9.74), $[Cd_2(HPen)_3(Pen)_2]^{3-}$ (log $\beta_{2,\,5,\,3}$ = 71.04), $[Cd_3(HPen)_2(Pen)_2]$ (log $\beta_{3,\,4,\,2}$ = 63.26), $[Cd_3(HPen)_4(Pen)_2]^{2-}$ (log $\beta_{3,\,6,\,4}$ = 93.54), $[Cd_4(HPen)_5(Pen)_2]^{2-}$ (log $\beta_{4,\,7,\,5}$ = 113.4), $[Cd_5(HPen)_6(Pen)_2]$ (log $\beta_{5,\,8,\,6}$ = 133.8). These formation constants were obtained for cadmium(II) and penicillamine complexation at 25 ºC in the ionic medium 0.2 mol dm^{-3} KNO_3, with $[Cd^{2+}]_{total}$ = 1 - 5 mmol dm^{-3} and 3-fold or more excess of penicillamine (*Ref.* 16).

The distribution diagrams in Figure S-2b were calculated with MEDUSA computer program (http://www.kemi.kth.se/medusa/). The full input file to MEDUSA is:

```
 3,  18,  3,  0     /HYDRA,  t=25 C
H+
Cd 2+
Pen 2-
CdPenH+            ,   16.39          1  1  1
Cd(Pen)2 2-        ,   20.27          0  1  2
Cd3(Pen)4H2        ,   63.26          2  3  4
Cd(Pen)2OH 3-      ,   9.74           -1  1  2
Cd2(Pen)5H3 3-     ,  71.04           3  2  5
Cd3(Pen)6H4 2-     ,   93.54           4  3  6
Cd5(Pen)8H6        ,   133.8          6  5  8
Cd4(Pen)7H5-       ,   113.4          5  4  7
Cd(OH)2            ,  -20.35          -2  1  0
Cd(OH)3-           ,  -33.3           -3  1  0
Cd(OH)4 2-         ,  -47.35          -4  1  0
Cd2OH 3+           ,  -9.39            -1  2  0
Cd4(OH)4 4+        ,  -32.85          -4  4  0
CdOH+              ,  -10.08          -1  1  0
HPen -             ,   10.42          1  0  1
H2Pen              ,   18.30          2  0  1
H3Pen +            ,   20.20          3  0  1
OH-                ,  -14.0           -1  0  0
Cd(OH)2(am)        ,  -13.73          -2  1  0
Cd(OH)2(c)         ,  -13.65          -2  1  0
CdO(c)             ,  -13.77          -2  1  0
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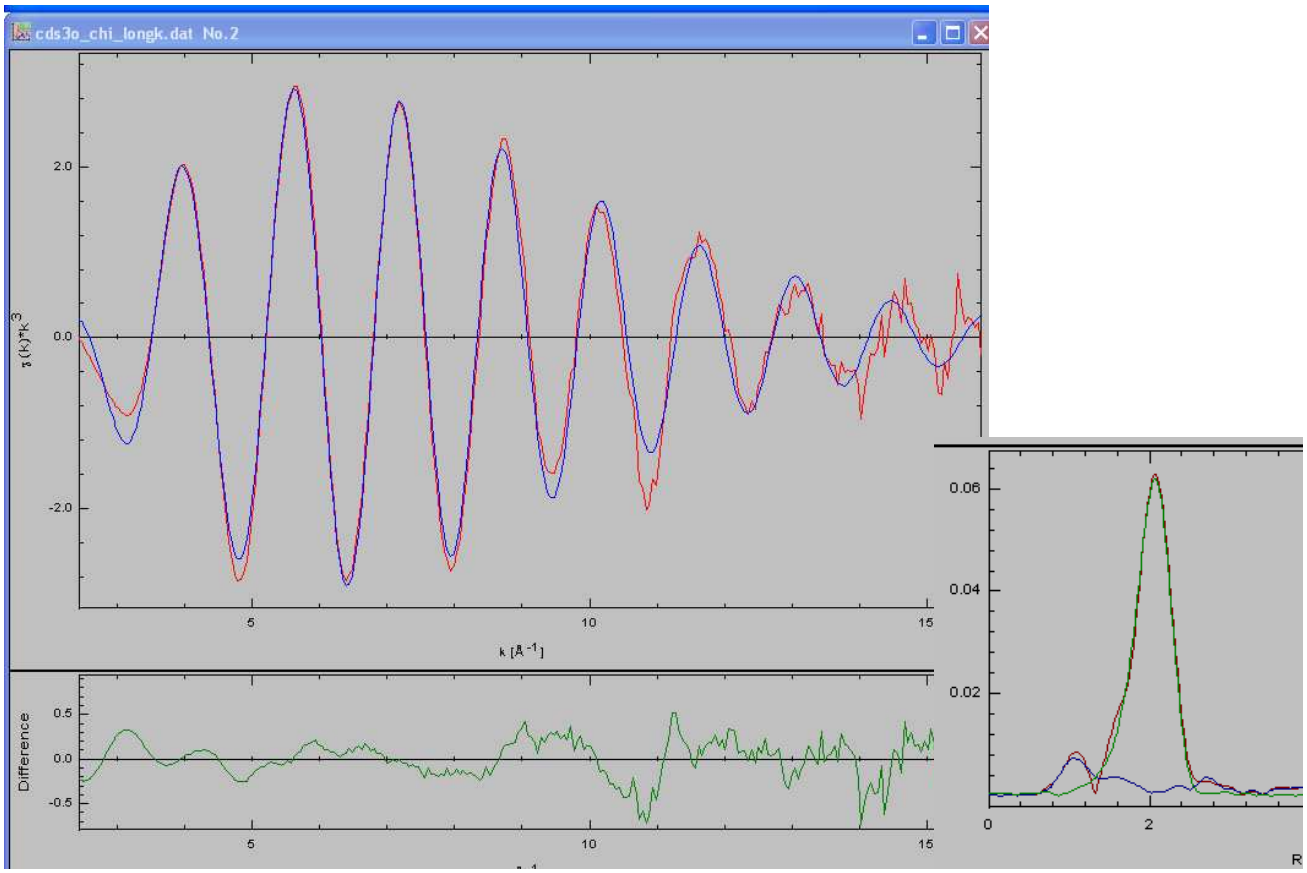
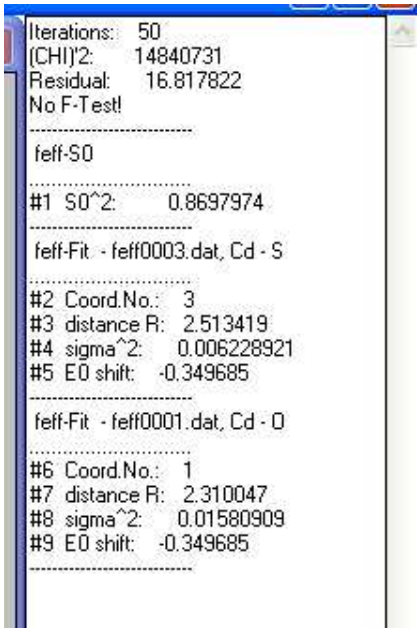




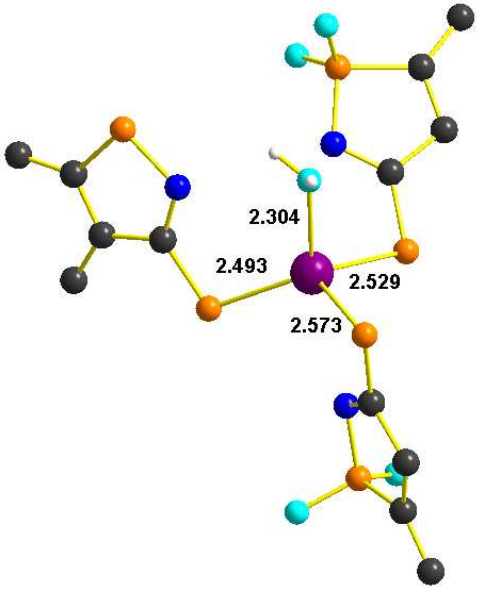
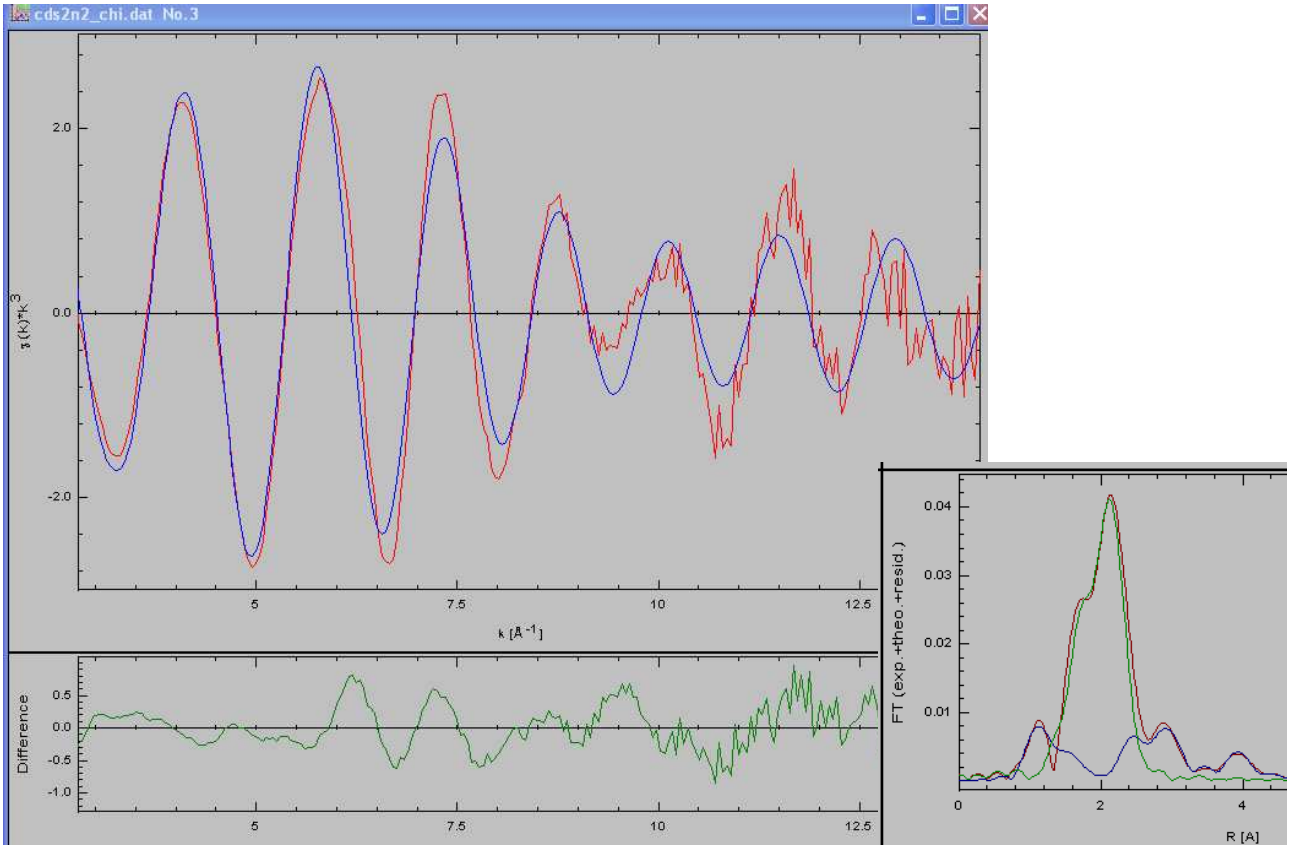
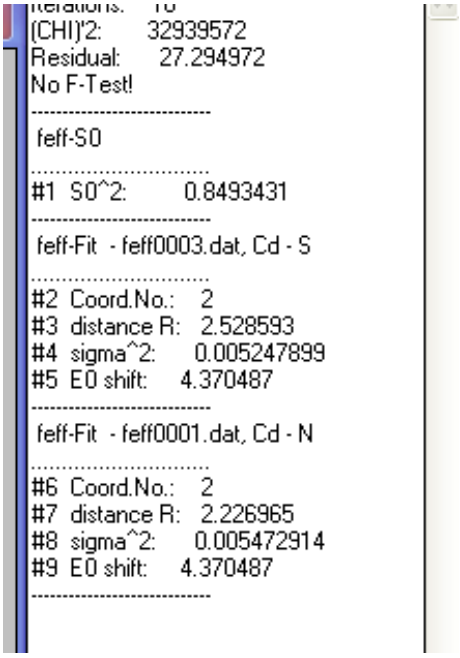


Figure S-3a. Least-squares curve-fitting of the k^3-weighted EXAFS spectrum of imidazolium tris(thiosaccharinato)aqua cadmate(II), (HIm)[Cd(tsac)$_3$(H$_2$O)], as CdS_3O model. For simulating the theoretical EXAFS oscillation, the atomic coordinates of its crystal structure were used in the ATOMS program to generate the FEFF input file.





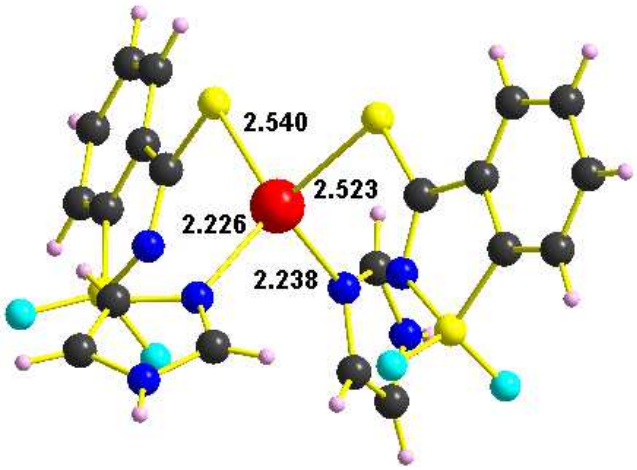


Figure S-3b. Least-squares curve-fitting of the k^3-weighted EXAFS spectrum of bis(thiosaccharinato)bis(imidazole) cadmium(II), $[Cd(tsac)_2(Im)_2]$, as CdS_2N_2 model. For simulating the theoretical EXAFS oscillation, the atomic coordinates of its crystal structure were used in the ATOMS program to generate the FEFF input file.

Table S-1. Total number of scans collected during the ^{113}Cd NMR measurements for Cd(II) – cysteine and penicillamine solutions, and the full width at half-height (FWHH) for the observed NMR signals

Cysteine ssolution (pH = 7.5)	No. scans	FWHH (Hz)	Solution (pH = 11.0)	No. scans	FWHH (Hz)
A1	3489	2320	**A2**	805	761
B1	736	945	**B2**	1040	271
C1	750	418	**C2**	658	190
D1	511	115	**D2**	605	157
E1	376	33	**E2**	537	136
F1	181	15	**F2**	539	21
G1	154	16	**G2**	550	17

Penicillamine solution (pH = 7.5)	No. scans	FWHH (Hz)	Solution (pH = 11.0)	No. scans	FWHH (Hz)
H1	4299	2120	**H2**	11348	77
I1	1531	1595	**I2**	1118	114
J1	750	805	**J2**	278	106
K1	626	447	**K2**	434	92
L1	500	55	**L2**	724	19
M1	141	14	**M2**	542	6
N1	353	38	**N2**	550	6

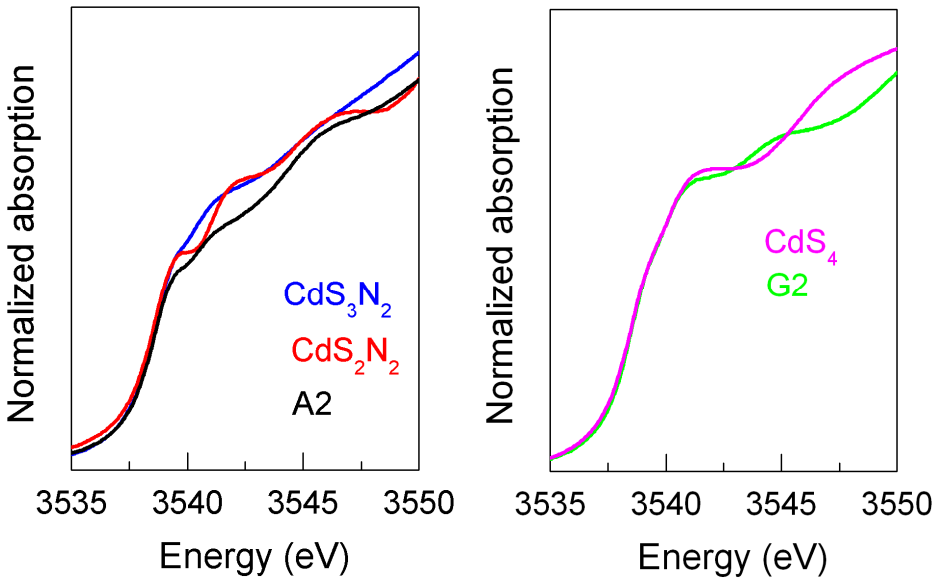


Figure S-4. Cd L_3-edge XANES spectra of cadmium(II) cysteine solutions **A2** and **G2** (pH = 11), compared with those of crystalline Cd(II) complexes with CdS_2N_2, CdS_3N_2 and CdS_4 geometries.

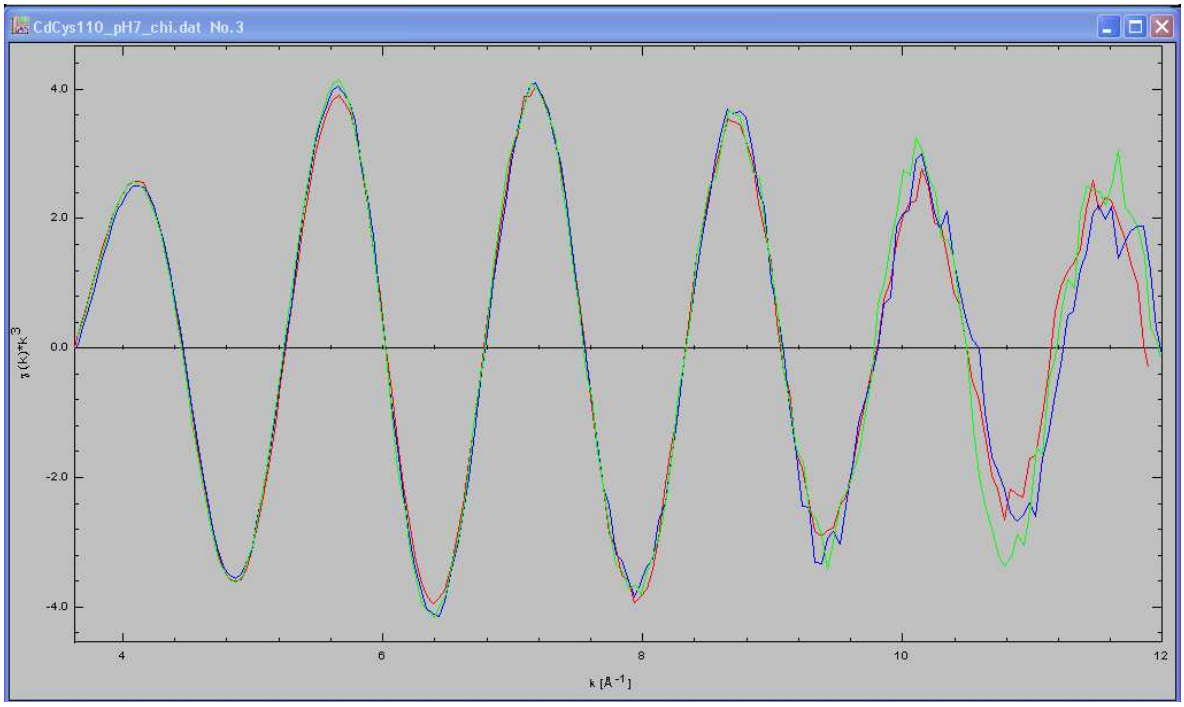


Figure S-5. Comparison between the k^3-weighted EXAFS spectra of cadmium(II) cysteine solutions **E1** (red), **F1** (blue) and **G1** (green) solutions (pH = 7.5).

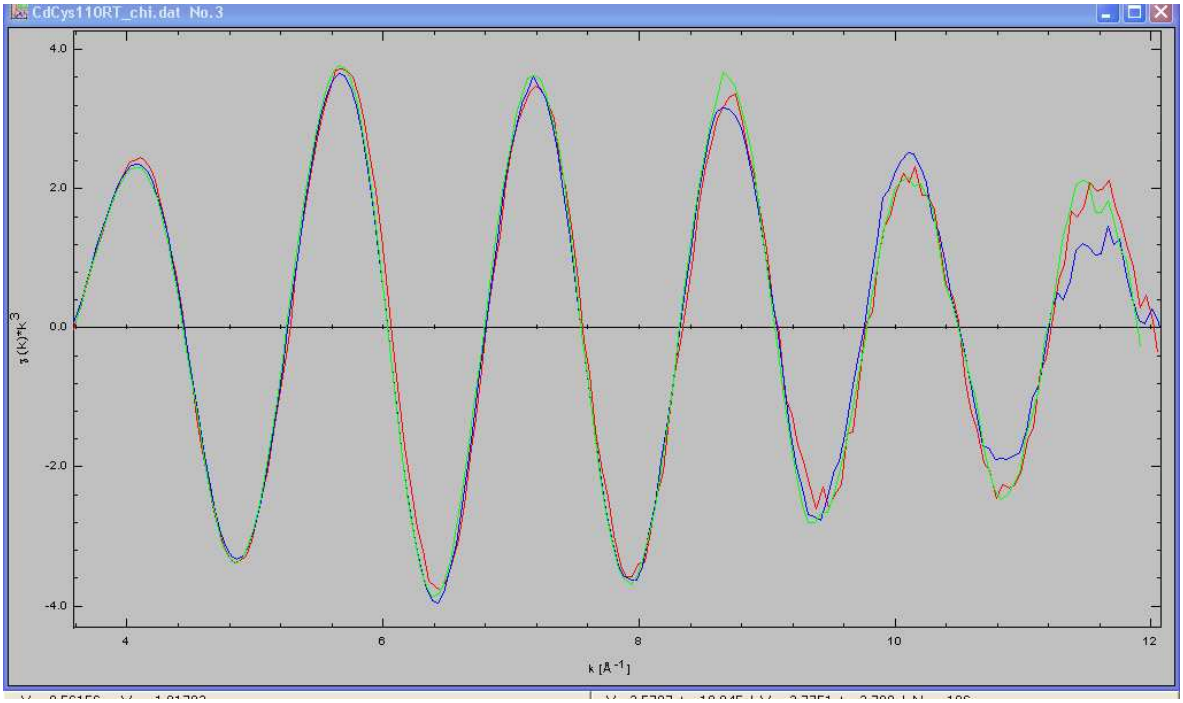


Figure S-6. Comparison between the k^3-weighted EXAFS spectra of cadmium(II) cysteine solutions **E2** (red), **F2** (blue) and **G2** (green) solutions (pH = 11.0).

a)

b)

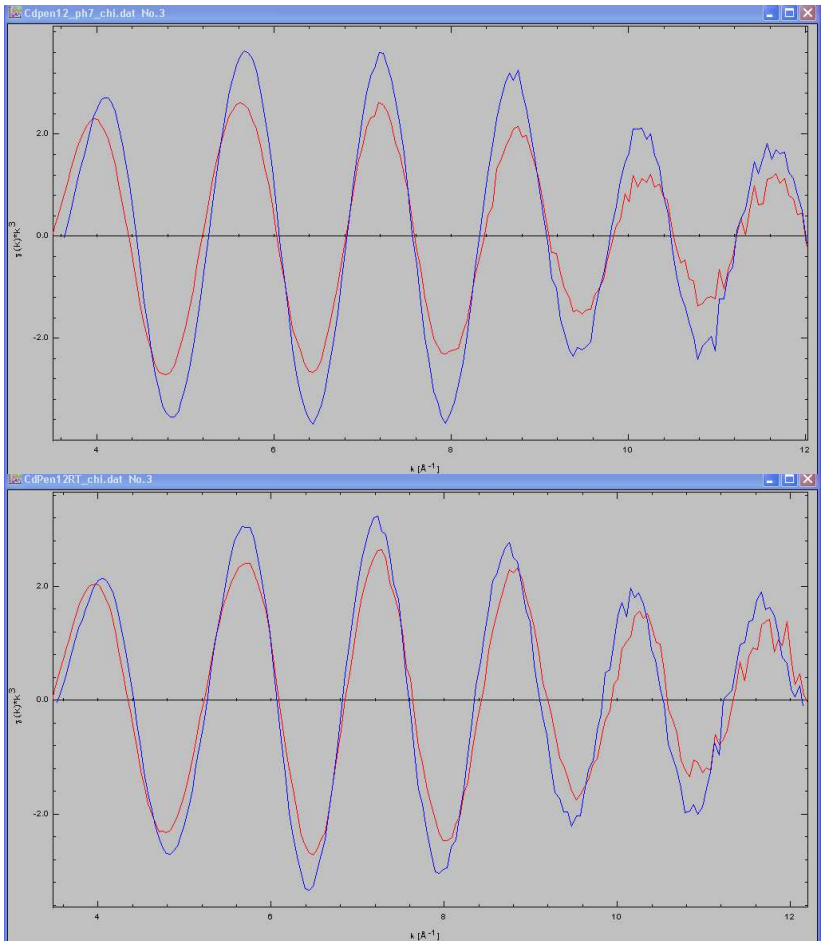


Figure S-7. Comparison between the k^3-weighted EXAFS spectra of cadmium(II) penicillamine solutions: *a*) **H1** (red) and **L1** (blue) (pH = 7.5); *b*) **H2** (red) and **L2** (blue) (pH = 11.0).

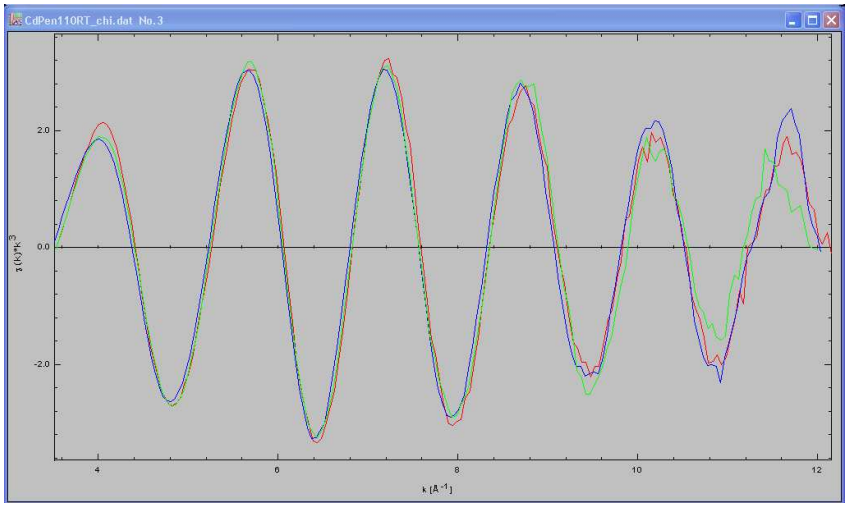
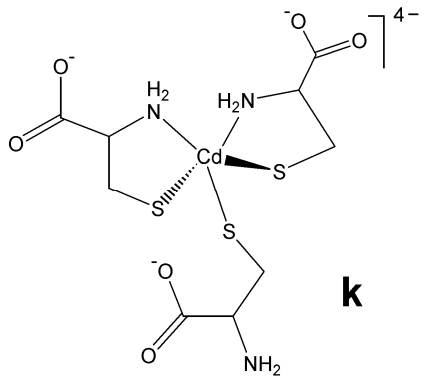
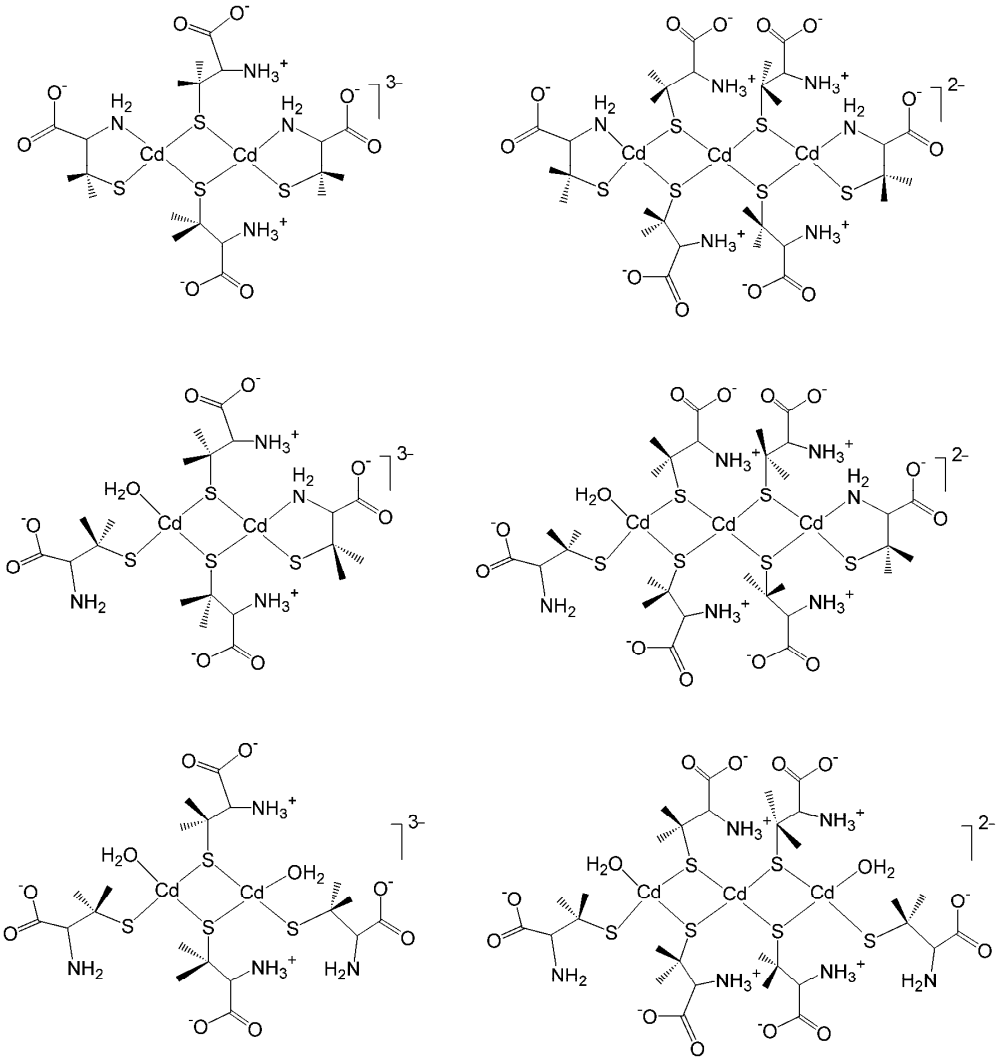


Figure S-8. Comparison between the k^3-weighted EXAFS spectra of cadmium(II) penicillamine solutions **L2** (red), **M2** (blue) and **N2** (green) solutions (pH = 11.0).



k

Scheme S-1. Structure **k** with CdS_3N_2 geometry does not seem to be a feasible structure for $[Cd(Cys)_3]^{4-}$ complex (see the text).



Scheme S-2. Possible structures for the polynuclear cadmium(II)-penicillamine complexes $[Cd_2(HPen)_3(Pen)_2]^{3-}$ (*left*) and $[Cd_3(HPen)_4(Pen)_2]^{2-}$ (*right*), proposed by Avdeef et al. (*Ref.* 16), to form between pH = 4 – 8 (see Figure S-2b).