

$\theta/2\theta$ scans $h = 0 \rightarrow 13$
 Absorption correction: $k = -17 \rightarrow 17$
 ψ scan (North *et al.*,
 1968) $l = -13 \rightarrow 13$
 $T_{\min} = 0.967$, $T_{\max} = 0.999$ 3 standard reflections
 6308 measured reflections every 100 reflections
 5976 independent reflections intensity decay: none
 3759 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F $w = 1/[\sigma^2(F_o) + 0.0019|F_o|^2]$
 $R = 0.053$ $(\Delta/\sigma)_{\max} = 0.001$
 $wR = 0.071$ $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 $S = 1.10$ $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
 3956 reflections Extinction correction: none
 343 parameters Scattering factors from
 H-atom parameters not *International Tables for*
 refined *Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

V1—O2	1.588 (3)	N7—C16	1.299 (4)
V1—O3	1.926 (3)	N7—C17	1.416 (4)
V1—O4	1.934 (2)	N8—C24	1.422 (4)
V1—N7	2.078 (3)	N8—C31	1.297 (4)
V1—N8	2.072 (3)	C17—C24	1.356 (5)
O2—V1—O3	108.1 (1)	O3—V1—N7	87.1 (1)
O2—V1—O4	109.2 (1)	O4—V1—N8	88.2 (1)
O2—V1—N7	105.5 (1)	N7—V1—N8	77.3 (1)
O2—V1—N8	103.6 (1)	N7—C17—C24	116.4 (3)
O3—V1—O4	88.4 (1)	N8—C24—C17	115.2 (3)

All H-atom positions were calculated geometrically.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1233). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
 Boucher, L. J. & Yen, T. F. (1968). *Inorg. Chem.* **7**, 2665–2667.
 Hoshina, G., Tsuchimoto, M., Ohba, S., Nakajima, K., Uekusa, H., Ohashi, Y., Ishida, H. & Kojima, M. (1998). *Inorg. Chem.* **37**, 142–145.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Mathew, M., Carty, A. J. & Palenik, G. J. (1970). *J. Am. Chem. Soc.* **92**, 3197–3198.
 Molecular Structure Corporation (1993). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

- Root, C. A., Hoeschele, J. D., Cornman, C. R., Kampf, J. W. & Pecoraro, V. L. (1993). *Inorg. Chem.* **32**, 3855–3861.
 Wang, X., Zhang, X. M. & Liu, H. (1995). *Polyhedron*, **14**, 293–296.

Acta Cryst. (1999). **C55**, 1453–1457

Aqua(benzo-15-crown-5)lithium-hexa- μ -iodotetracopper-benzo-15-crown-5 (2/1/2), bis[bis(benzo-15-crown-5)caesium] hexa- μ -iodotetracopper and μ -aqua-bis[aqua(18-crown-6)sodium] hexa- μ -iodotetracopper†

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Abstract

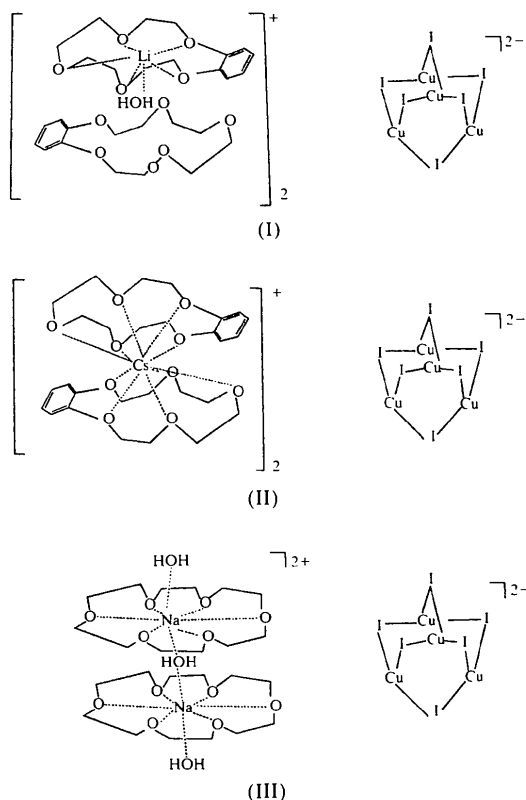
The title compounds, $[\text{Li}(\text{C}_{14}\text{H}_{20}\text{O}_5)(\text{H}_2\text{O})]_2[\text{Cu}_4\text{I}_6] \cdot 2\text{C}_{14}\text{H}_{20}\text{O}_5$, $[\text{Cs}(\text{C}_{14}\text{H}_{20}\text{O}_5)_2]_2[\text{Cu}_4\text{I}_6]$ and $[\text{Na}_2(\text{C}_{12}\text{H}_{24}\text{O}_6)_2(\text{H}_2\text{O})_3][\text{Cu}_4\text{I}_6]$, respectively, all show similar $[\text{Cu}_4\text{I}_6]^{2-}$ clusters disordered about a center of symmetry. The Cu atoms are three-coordinate, with an average Cu—I distance of 2.596 (3) \AA . Alkali-bound crown-ether groups serve as counter-ions. The three solid materials display identical emission in the visible when excited in the ultraviolet. Calculations of the atomic contributions to frontier orbitals show the highest occupied molecular orbital (HOMO) to be based primarily on contributions from four of the six I atoms and the lowest unoccupied molecular orbital (LUMO) to be primarily copper-based and involving contributions from the four Cu atoms.

Comment

Copper halide complexes adopt a wide variety of stoichiometries in the formation of neutral (Caulton *et al.*, 1990) and anionic clusters of diverse form (Jagner & Helgesson, 1991; Hu & Holt, 1994*a,b,c,d*; Nurtaeva & Holt, 1998*a,b*). Many of these solid-state complexes have been shown to emit in the visible range when excited in the ultraviolet (Rath & Holt, 1985; Rath *et al.*, 1985), however, quenching effects due to delocalized π systems in the accompanying cation may interfere with the observation of emission (Tompkins *et al.*, 1987; Hu *et al.*, 1995). We have prepared a series of copper iodide

† Systematic nomenclature: benzo-15-crown-5 is 2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-15,17,19-triene and 18-crown-6 is 1,4,7,10,13,16-hexaazacyclooctadecane.

complexes with crown-ether-complexed alkali metals and have found three of them to crystallize with the [Cu₄I₆]²⁻ motif and to display similar emissions in the visible.



Aqua(benzo-15-crown-5)lithium-hexa- μ -iodotetra-copper-benzo-15-crown-5 (2/1/2), (I), bis[bis(benzo-15-crown-5)caesium] hexa- μ -iodotetra-copper, (II), and μ -

aqua-bis[aqua(18-crown-6)sodium] hexa- μ -iodotetra-copper, (III), all show the [Cu₄I₆]²⁻ cluster to be disordered about a crystallographic center of symmetry (Fig. 1). However, the eight copper positions observed at 50% occupancy may be seen clearly to belong to two different [Cu₄I₆]²⁻ clusters involving a tetrahedron of Cu atoms bridged on each edge by the six I atoms. The Cu^I atoms are three-coordinate, with average Cu—I distances of 2.612 (3), 2.614 (3) and 2.561 (2) Å in (I), (II) and (III), respectively. Non-bonded Cu··Cu distances are 2.819 (4), 2.810 (4) and 2.752 (5) Å in (I), (II) and (III), respectively, just outside the range of Cu··Cu distances considered interactive. These details are consistent with those reported for triphenylmethylphosphonium [Cu₄I₆]²⁻ (Bowmaker *et al.*, 1976) and K₇(12-crown-4)₆[Cu₄I₆][Cu₈I₁₃] (Rath & Holt, 1985).

While structures (I) and (II) might be suspected to be isostructural, based on the similarity of the unit-cell dimensions and space group, examination of their packing diagrams shows them to differ in an interesting way. The Cs atom of (II), which forms a sandwich with two benzo-15-crown-5 rings [ten Cs—O distances average 3.230 (5) Å], is replaced by Li—OH₂ in (I), with the Li atom in the plane of the five O atoms of one benzo-15-crown-5 ring [average Li—O_{crown} 2.31 (2) Å] and additionally bonded to the oxygen (O99) of a water molecule [Li—O_{water} 1.94 (2) Å]. The two H atoms of the water molecule (O99) each form a hydrogen bond to the second benzo-15-crown-5 ring (H99A··O30 2.172 and H99B··O24 2.244 Å) (Fig. 2). In (II), the magnitudes of the *U*_{eq} values for C25, C26 and O27 indicate disorder for these positions. In (III), the Na atom is found in the center of an 18-crown-6 ring [average Na—O_{crown} 2.746 (7) Å] and is bonded to a terminal (O21) water molecule [Na—O_{terminal} 2.257 (7) Å]. A second water molecule close to a center of symmetry bridges two sodium(18-crown-6)-(HOH) groups. Disorder of this O atom (O22) about

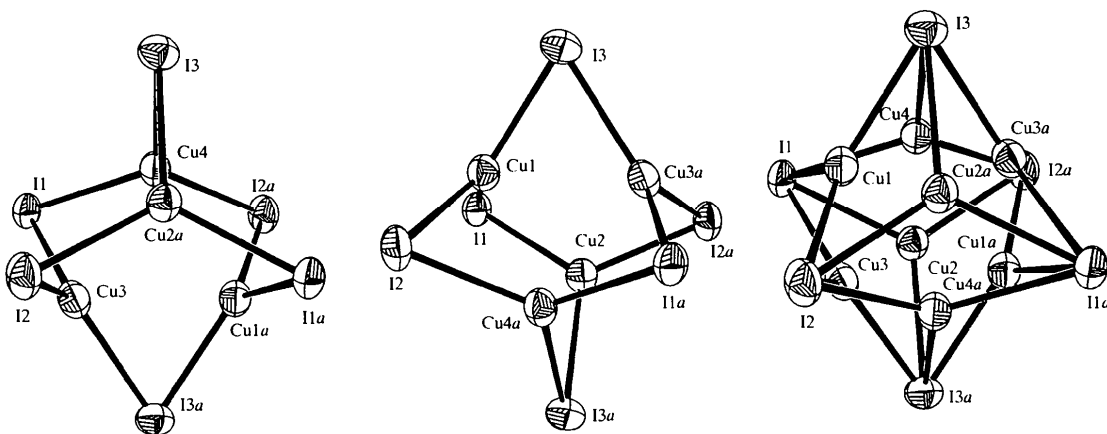


Fig. 1. View of the [Cu₄I₆]²⁻ cluster of (I) showing two ordered clusters and the disordered composite with a center of symmetry. Displacement ellipsoids are shown at the 50% probability level.

the center of symmetry is evident in the shape of the displacement parameters [$\text{Na}-\text{O}_{\text{bridging}} 2.279(3) \text{ \AA}$]. The distances between alkali metals and crown-ether O atoms fall close to the sums of the appropriate ionic radii for appropriate metal coordination numbers: Cs (1.81 \AA) + O (1.36 \AA) = 3.17 \AA , Na (2.18 \AA) + O = 2.54 \AA , and Li (0.76 \AA) + O = 2.12 \AA (Shannon, 1976).

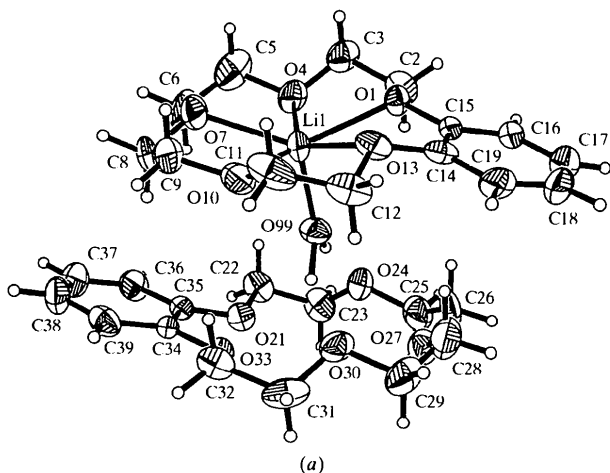


Fig. 2. Comparison views of (a) the lithium cation of (I) and (b) the caesium cation of (II). Displacement ellipsoids are shown at the 50% probability level.

The three solid materials display emission in the visible at 520 nm when excited in the ultraviolet at 300 nm. This is consistent with the expectation that clusters of similar and non-interfering crystallographic symmetry should display similar emission. Calculation of the atomic contribution (GAUSSIAN94; Frisch *et al.*, 1995) to frontier orbitals showed the HOMO (highest occupied molecular orbital) level to be dominated by P_y and P_z orbitals associated with four of the I atoms, whereas the LUMO (lowest unoccupied molecular orbital) level

is principally copper-based (S , P_x , P_y and P_z) and involves all four Cu atoms.

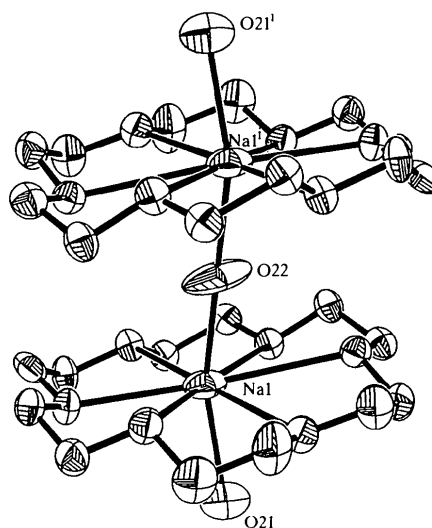


Fig. 3. View of the dimeric sodium cation of (III). Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (i) $1-x, 2-y, 1-z$.]

Experimental

For the preparation of (I), a saturated solution of LiI in water (5 ml) was added to a mixture of CuI (2 mmol, 0.382 g), benzo-15-crown-5 (1.5 mmol, 0.402 g) and ascorbic acid (0.213 g) [to retard oxidation of copper(I)] in acetone (40 ml). The resulting suspension was heated under reflux until all solids had dissolved completely (4 h). The solution was allowed to cool slowly and yellow plates were observed to form after two days. For the preparation of (II), a saturated solution of CsI in water (10 ml) was added to CuI (2 mmol, 0.382 g), benzo-15-crown-5 (2 mmol, 0.536 g) and ascorbic acid (0.213 g) in acetone (40 ml). The resulting mixture was heated under reflux until a clear solution resulted (2 h). The solution was allowed to cool slowly. After two days, long colorless needles of the known compound CsCu_2I_3 (Jouini *et al.*, 1980) were observed to form, however, after 24 h, yellow prisms of (II) were found. For the preparation of (III), a mixture of CuI (2 mmol, 0.382 g), 18-crown-6 (2 mmol, 0.528 g) and NaI (3 mmol, 0.450 g) was dissolved in water (3 ml) to which acetone (40 ml) was added and the resulting solution heated under reflux for 6 h until complete dissolution of the CuI. Ascorbic acid (0.213 g) was added to preserve the +1 oxidation state of copper. The resulting yellow solution was filtered and allowed to stand for three days whereupon yellow-green rods appeared.

Compound (I)

Crystal data

$[\text{Li}(\text{C}_{14}\text{H}_{20}\text{O}_5)(\text{H}_2\text{O})]_2 \cdot$
 $[\text{Cu}_4\text{I}_6] \cdot 2\text{C}_{14}\text{H}_{20}\text{O}_5$
 $M_r = 2138.6$
 Monoclinic
 $P2_1/c$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25
 reflections
 $\theta = 15.0\text{--}29.6^\circ$

$a = 11.081 (8) \text{ \AA}$
 $b = 16.103 (10) \text{ \AA}$
 $c = 22.211 (14) \text{ \AA}$
 $\beta = 90.38 (3)^\circ$
 $V = 3963 (5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.787 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens P4 four-circle
 diffractometer
 θ -2 θ scans
 Absorption correction:
 ψ scan (XEMP; Siemens,
 1991)
 $T_{\min} = 0.62, T_{\max} = 0.65$
 14 937 measured reflections
 11 547 independent
 reflections

Refinement

Refinement on F^2
 $R(F) = 0.073$
 $wR(F^2) = 0.197$
 $S = 0.972$
 11 547 reflections
 430 parameters
 H-atom parameters
 constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0724P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected bond lengths (Å) for (I)

Cu1—I3	2.574 (3)	Cu3—Cu2'	2.784 (4)
Cu1—I2	2.599 (3)	Cu3—Cu1'	2.818 (4)
Cu1—I1	2.628 (3)	Cu3—Cu4	2.894 (3)
Cu1—Cu4'	2.773 (4)	Cu4—I2'	2.598 (3)
Cu1—Cu3'	2.818 (4)	Cu4—I1	2.609 (3)
Cu1—Cu2	2.922 (4)	Cu4—I3	2.622 (3)
Cu2—I2'	2.586 (3)	Cu4—Cu1'	2.773 (4)
Cu2—I1	2.596 (3)	Cu4—Cu2'	2.794 (3)
Cu2—I3'	2.615 (3)	Li1—O99	1.937 (19)
Cu2—Cu3'	2.784 (4)	Li1—O7	2.251 (19)
Cu2—Cu4'	2.794 (3)	Li1—O1	2.281 (18)
Cu3—I1	2.608 (3)	Li1—O10	2.300 (19)
Cu3—I3'	2.645 (3)	Li1—O4	2.30 (2)
Cu3—I2	2.659 (3)	Li1—O13	2.41 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.**Compound (II)****Crystal data**

$[\text{Cs}(\text{C}_{14}\text{H}_{20}\text{O}_5)_2]_2[\text{Cu}_4\text{I}_6]$
 $M_r = 2354.6$
 Monoclinic
 $P2_1/c$
 $a = 10.896 (4) \text{ \AA}$
 $b = 16.277 (5) \text{ \AA}$
 $c = 22.638 (7) \text{ \AA}$
 $\beta = 91.37 (2)^\circ$
 $V = 4014 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.950 \text{ Mg m}^{-3}$
 D_m not measured

$\mu = 3.447 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Plate
 $0.20 \times 0.20 \times 0.15 \text{ mm}$
 Yellow

4290 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$
 $\theta_{\text{max}} = 30.01^\circ$
 $h = -15 \rightarrow 15$
 $k = -1 \rightarrow 22$
 $l = -1 \rightarrow 31$
 3 standard reflections
 every 97 reflections
 intensity decay: none

$(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.597 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.536 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL97
 Extinction coefficient:
 0.0033 (3)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Data collection

Syntex P4 four-circle
 diffractometer
 θ -2 θ scans
 Absorption correction:
 ψ scan (XEMP; Siemens,
 1991)
 $T_{\min} = 0.58, T_{\max} = 0.71$
 14 076 measured reflections
 11 572 independent
 reflections

Refinement

Refinement on F^2
 $R(F) = 0.064$
 $wR(F^2) = 0.181$
 $S = 0.960$
 11 572 reflections
 421 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0704P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

4483 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.0611$
 $\theta_{\text{max}} = 30.01^\circ$
 $h = -1 \rightarrow 15$
 $k = -1 \rightarrow 22$
 $l = -31 \rightarrow 31$
 3 standard reflections
 every 97 reflections
 intensity decay: none

$(\Delta/\sigma)_{\text{max}} = 0.009$
 $\Delta\rho_{\text{max}} = 0.985 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.931 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL97
 Extinction coefficient:
 0.00119 (14)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 2. Selected bond lengths (Å) for (II)

Cu1—I3	2.579 (2)	Cu3—Cu4'	2.807 (3)
Cu1—I2	2.591 (2)	Cu4—I1	2.611 (3)
Cu1—I1	2.633 (3)	Cu4—I2	2.622 (3)
Cu1—Cu4'	2.762 (3)	Cu4—I3'	2.672 (3)
Cu1—Cu2'	2.789 (3)	Cu4—Cu1'	2.762 (3)
Cu1—Cu3	2.933 (4)	Cu4—Cu3'	2.807 (3)
Cu2—I3	2.580 (3)	Cs1—O27	3.145 (12)
Cu2—I2	2.589 (3)	Cs1—O10	3.148 (6)
Cu2—I1'	2.653 (3)	Cs1—O30	3.211 (7)
Cu2—Cu3'	2.762 (4)	Cs1—O13	3.212 (6)
Cu2—Cu1'	2.789 (3)	Cs1—O24	3.220 (8)
Cu2—Cu4	2.925 (4)	Cs1—O4	3.233 (6)
Cu3—I1'	2.561 (3)	Cs1—O1	3.237 (6)
Cu3—I3'	2.634 (3)	Cs1—O21	3.267 (6)
Cu3—I2	2.643 (3)	Cs1—O7	3.307 (9)
Cu3—Cu2'	2.762 (4)	Cs1—O33	3.323 (6)

Symmetry code: (i) $2 - x, -y, 1 - z$.**Compound (III)****Crystal data**

$[\text{Na}_2(\text{C}_{12}\text{H}_{24}\text{O}_6)_2(\text{H}_2\text{O})_3]\text{-}$
 $[\text{Cu}_4\text{I}_6]$
 $M_r = 1644.2$
 Monoclinic
 $P2_1/c$
 $a = 11.303 (2) \text{ \AA}$
 $b = 13.926 (2) \text{ \AA}$
 $c = 15.268 (3) \text{ \AA}$
 $\beta = 96.95 (1)^\circ$
 $V = 2385.4 (7) \text{ \AA}^3$
 $Z = 2$
 $D_x = 2.289 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens P4 four-circle
 diffractometer

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 42
 reflections
 $\theta = 4.75\text{--}12.47^\circ$
 $\mu = 5.712 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Rod
 $0.10 \times 0.10 \times 0.05 \text{ mm}$
 Yellow

2522 reflections with
 $I > 2\sigma(I)$

θ -2 θ scans
Absorption correction:
 ψ scan (XEMP; Siemens,
1991)
 $T_{\min} = 0.60$, $T_{\max} = 0.66$
8507 measured reflections
6945 independent reflections

$R_{\text{int}} = 0.0575$
 $\theta_{\max} = 30^\circ$
 $h = -1 \rightarrow 15$
 $k = -1 \rightarrow 19$
 $l = -21 \rightarrow 21$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.047$
 $wR(F^2) = 0.104$
 $S = 0.852$
6945 reflections
252 parameters
H-atom parameters
constrained
 $w = 1/[\sigma^2(F) + (0.0008)F^2]$
 $(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.578 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.720 \text{ e } \text{\AA}^{-3}$
Extinction correction:
SHELXL97
Extinction coefficient:
0.00012 (7)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 3. Selected bond lengths (\AA) for (III)

I1—Cu6	2.552 (2)	I3—Cu5'	2.562 (2)
I1—Cu7	2.568 (2)	I3—Cu6'	2.571 (2)
I1—Cu4	2.579 (2)	Na1—O21	2.257 (7)
I1—Cu5	2.588 (2)	Na1—O22	2.279 (3)
I2—Cu6'	2.545 (2)	Na1—O1	2.564 (6)
I2—Cu5	2.551 (2)	Na1—O4	2.628 (7)
I2—Cu7'	2.568 (2)	Na1—O16	2.663 (7)
I2—Cu4	2.593 (2)	Na1—O10	2.839 (7)
I3—Cu4	2.5217 (19)	Na1—O7	2.886 (7)
I3—Cu7	2.538 (2)	Na1—O13	2.897 (7)

Symmetry code: (i) $-x, 2 - y, -z$.

Extinction was refined for all three structures but was minimal. Atoms Cu1—Cu4 in (I) and (II), and atoms Cu4—Cu7 in (III) all have 50% site occupancy.

For all compounds, data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1990)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1087). Services for accessing these data are described at the back of the journal.

References

- Bowmaker, G. A., Clark, G. R. & Yuen, D. K. P. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2329–2351.
- Caulton, K. G., Davies, G. & Holt, E. M. (1990). *Polyhedron*, pp. 2319–2351.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challalcombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andrews, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. L., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. & Pople, J. A. (1995). *GAUSSIAN94*. Revision A1. Gaussian Inc., Pittsburgh, PA, USA.
- Hu, G. & Holt, E. M. (1994a). *Acta Cryst.* **C50**, 1212–1214.
- Hu, G. & Holt, E. M. (1994b). *Acta Cryst.* **C50**, 1576–1578.
- Hu, G. & Holt, E. M. (1994c). *Acta Cryst.* **C50**, 1578–1580.

- Hu, G. & Holt, E. M. (1994d). *Acta Cryst.* **C50**, 1890–1892.
- Hu, G., Mains, G. J. & Holt, E. M. (1995). *Inorg. Chim. Acta*, **240**, 559–565.
- Jagner, S. & Helgesson, G. (1991). *Advances in Inorganic Chemistry*, edited by A. G. Syles, Vol. 37, pp. 1–45. San Diego: Academic Press.
- Jouini, N., Guen, L. & Tournoux, M. (1980). *Rev. Chem. Miner.* **17**, 486–492.
- Nurtaeva, A. & Holt, E. M. (1998a). *Acta Cryst.* **C54**, 594–597.
- Nurtaeva, A. & Holt, E. M. (1998b). *Acta Cryst.* **C54**, 597–600.
- Rath, N. P. & Holt, E. M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 665–667.
- Rath, N. P., Holt, E. M. & Tanimura, K. (1985). *Inorg. Chem.* **24**, 3934–3938.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–754.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tompkins, J. A., Maxwell, J. L. & Holt, E. M. (1987). *Inorg. Chim. Acta*, **127**, 1–7.

Acta Cryst. (1999). **C55**, 1457–1460

Tetraaqua(2,2'-bipyridyl-*N,N'*)cadmium(II) sulfate and catena-poly[[[diaqua(2,2'-bipyridyl-*N,N'*)cadmium(II)]- μ -(sulfato-O:O')] hydrate]

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Abstract

In both title compounds, $[\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]\text{SO}_4$, (I), and $[\text{Cd}(\text{SO}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, (II), the Cd^{II} ion is octahedrally coordinated. In (I), the Cd^{2+} ion is coordinated to a bipyridine and four water molecules, the structure being monomeric and strictly ionic in nature, and in (II), to a bipyridine, two water molecules