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Flexible Square Supramolecular Rings with Hydrogen-Bonded Bushing in Solid-State Oxalurate Complexes: Versatility of the Oxalurate Ligand in Covalent and Noncovalent Binding

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Isotypic pseudooctahedral complexes of Co, Ni, and Cu with two chelating oxalurate ligands and two water molecules, *trans*-[M(oxalurate)$_2$(H$_2$O)$_2$], have been synthesized and isolated by a novel progressive crystallization technique. Diffraction analyses reveal that the three complexes form isotypic solid-state structures in which the molecular connectivity and complex network of noncovalent interactions are qualitatively identical throughout the series. The oxalurate groups form unbounded chains through two different self-recognition patterns—a typical DA–AD motif and an unusual DDA′–A′DD form (D = hydrogen bond donor, A′ = double acceptor). The unsymmetrical oxalurate group possesses the topological properties necessary to form aggregates of higher symmetry, and the “M(oxalurate)$_2$” fragments form a rhombic 2-D motif with hydrogen-bonded corners and with hydrogen-bond acceptors directed to the inside of the cyclic aggregate. The 2-D net is stacked to form a channeled 3-D structure, in which the coordinated aqua ligands form the principal interlayer interactions. The slanted channels are occupied by the axial waters and by waters of crystallization, which are hydrogen bonded to the channel walls to form an ordered bushing. The extensive 3-D hydrogen-bonded superstructure is flexible enough to accommodate the distortion produced by the Jahn–Teller effect in the copper compound without requiring a qualitative structural change. The bonds affected by Jahn–Teller distortion in the Cu complex [Cu–O = 2.3788(15) Å] are significantly longer than their analogues in the Co and Ni complexes [Co–O = 2.175(2), Ni–O = 2.094(9) Å].

Introduction

For some years we have been studying coordination complexes of polyfunctional ligands—largely organic moieties with several functional groups—with the principal aim of creating constrained environments around transition-metal centers. Because of the presence of the functional groups, polyfunctional ligands are capable of entering into relatively strong interactions with their environments in the solid state, thus leading to forces that can in principle countermand the natural stereochemical preferences of a d-block element. The functional groups used so far have been selected for their hydrogen-bonding capability, as this represents the strongest class of noncovalent, nonionic interactions. Our work in this area has been directed largely to the study of the response of the transition metal to its constrained environment, for example, in solid solutions of Jahn−Teller-active saccharinate or nicotinato complexes[1,2] in non-Jahn−Teller hosts or in solids formed by complexes of isocyanurate,[3] in which an aggregate structure formed by cyanurate moieties is observed to be structurally dominant, producing a flexible molecule in the solid state.[4] Apart from the main focus of this work, however, several instances of interesting packing patterns and ligand dominance have arisen, suggesting that at least some of the ligands that have been used and some of the constraining environments that have been observed about transition-metal complexes may be robust enough to merit further study in and of themselves. In fact, the study of known ligands or the design of new ligands with several possible coordination sites and with the ability to interact with their surroundings, for instance through hydrogen bonds,

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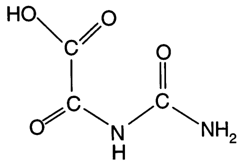

Figure 1. Oxaluric acid.

is a very active field of research due to the possibility of forming supramolecular aggregates[5] with potential applications in diverse areas including the currently active field of nanotechnology.[6]

Oxaluric acid, or oxalylurea, Figure 1, is the condensation product of oxalic acid and urea, and its hydrolysis produces those two compounds. It is a relatively small entity and possesses topological properties that should make it a versatile ligand from the structural point of view.

Deprotonated oxalurate possesses four oxygen atoms that can serve as hydrogen-bond acceptors along with two amine functions that can serve as hydrogen-bond donors. In addition one or more of six different atoms can bind to transition-metal centers in any of at least three distinct coordination modes, namely, chelating, terminal, or bridging coordination. Beyond that, the possibility of rotation about any of several single bonds within oxalurate can produce multiple conformations, some of them planar. Thus, this polyfunctional moiety can in theory participate in a wide variety of metal—ligand and intermolecular interactions. Although the ligand itself lacks nontrivial symmetry, its topology in principle permits it to form supramolecular structures with higher symmetry—a phenomenon known for urea and thiourea and whose exploitation has been viewed as a challenge in the currently growing field of supramolecular engineering.[7] In addition, urea, urea derivatives, and oxalyl amides, organic compounds related to oxalylurea, are being studied as gelators due to their hydrogen-bonding potential. Oxaluric acid is well-known in other contexts, as it is the final product of the potentially mutagenic oxidation of guanine.[8,9] Despite its interest in biochemistry and its potential as a ligand in coordination and supramolecular chemistry, little structural information has been presented on oxaluric acid and oxalurate and their complexes.

To our knowledge, there have been just two structural studies of crystals containing oxalurate.[10,11] No structural characterizations of transition-metal complexes of oxalurate have been published to date.

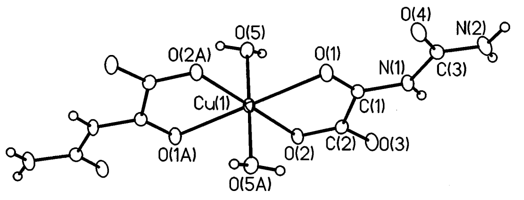

Figure 2. Perspective drawing of compound **4**. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

We report here the preparation and structural characterization of oxalurate complexes of three first-row transition metals, Co(II), Ni(II), and Cu(II). The three are isotypic in the solid state, despite significant local shape variations resulting from the Jahn—Teller effect in the copper complex. The structural type of the three possesses a rich network of intermolecular interactions, some of which arise from self-recognition of the oxalurate ligands, leading to interesting 1-D, 2-D, and 3-D supramolecular aggregates.

Results and Discussion

The reaction of Na(oxalurate), **1**, with Co(II), Ni(II), and Cu(II) salts produces the complexes *trans*-[M(oxalurate)$_2$(H$_2$O)$_2$] [M = Co (**2**), Ni (**3**), and Cu (**4**)], which were isolated and characterized by a variety of techniques. Crystals of the compounds were obtained by very slow procedures. For compounds **2** and **4** the procedure involved the formation of the oxalurate ligand by slow hydrolysis of the parabanate salt. Crystals of compound **3** were obtained directly, via the diffusion of a solution of nickel nitrate into a solution of sodium oxalurate through a layer of 2-methyl-2,4-pentanediol, which slowed the diffusion process.

The structures of compounds **2**—**4** were determined by X-ray diffraction. Figure 2 is a drawing of *trans*-[Cu(oxalurate)$_2$(H$_2$O)$_2$]·2H$_2$O, **4**. Complexes **2** and **3** have a qualitatively similar appearance. Table 1 collects the more relevant crystallographic data for the compounds, and Table 2 collects the main distances and angles, showing the differences among compounds **2**—**4**.

The three structures are isotypic. In the solid state, the metal atom resides on a crystallographic center of symmetry. It is surrounded by two water molecules in the apical positions, and by two chelating oxalurate ligands, giving a total of six ligated oxygen atoms forming a pseudooctahedral coordination environment. Oxalurate chelates through the carbonyl oxygen of the amide function and one oxygen atom of the deprotonated carboxylate, leaving the second partial-charge-bearing oxygen of the carboxylate pendant. As usual, the angle subtended by the chelate, which is ~80° in all cases, is the only *cis* angle that deviates significantly from 90°.

The M—O distances are unexceptional[12] on the whole and follow the well-known trends for first-row transition-metal

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Table 1. Crystallographic Data for $[M(oxalurate)_2(H_2O)_2]\cdot 2H_2O$ (M = Co (**2**), Ni (**3**), Cu (**4**))

	2	**3**	**4**
empirical formula	$CoC_6O_{12}N_4H_{14}$	$NiC_6O_{12}N_4H_{14}$	$CuC_6O_{12}N_4H_{14}$
fw	393.14	392.92	397.75
λ, Mo Kα (Å)	0.71073	0.71073	0.71073
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	1	1
temp (K)	223(2)	298(2)	148(2)
a (Å)	5.2969(6)	5.2699(6)	5.2584(8)
b (Å)	6.9893(13)	7.0130(11)	6.8332(15)
c (Å)	10.2575(19)	10.2911(13)	10.314(2)
α (deg)	71.983(16)	70.886(9)	72.69(2)
β (deg)	80.572(14)	79.954(10)	83.39(2)
γ (deg)	70.882(12)	71.499(9)	71.266(16)
V (Å^3)	340.38(10)	339.74(8)	334.99(11)
ρ_{calcd} (g$\cdot$cm^{-3})	1.918	1.920	1.972
μ (cm^{-1})	13.4	15.1	17.1
R1^a [$I > 2\sigma(I)$]	0.0448	0.0854	0.0282
wR2^b (all data)	0.1190	0.2169	0.0725

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$; $P = (F_o^2 + 2F_c^2)/3$; weight parameters a and b are given in the Supporting Information.

Table 2. Selected Distances (Å) and Angles (deg) for $[M(oxalurate)_2(H_2O)_2]\cdot 2H_2O$ (M = Co (**2**), Ni (**3**), Cu (**4**))

	distances, Å		
	Co	Ni	Cu
M−O(1)	2.175(2)	2.094(9)	2.3788(15)
M−O(2)	2.050(2)	1.996(10)	1.9567(15)
M−O(5)	2.037(2)	2.039(10)	1.9611(16)
C1−O(1)	1.217(4)	1.223(15)	1.218(3)
C2−O(2)	1.267(4)	1.277(18)	1.269(3)
C2−O(3)	1.227(4)	1.189(16)	1.228(2)

	angles, deg		
	Co	Ni	Cu
O(2)−M−O(5)	92.34(10)	91.8(4)	92.18(7)
O(2)−M−O(1)	77.96(9)	80.2(4)	76.56(6)
O(5)−M−O(1)	88.76(10)	88.5(4)	86.88(6)
M−O(1)−C(1)	111.3(2)	111.8(9)	106.20(13)
M−O(2)−C(2)	116.8(2)	119.1(9)	121.67(13)
O(1)−C(1)−C(2)	119.8(3)	119.6(13)	120.65(18)
O(2)−C(2)−C(1)	113.8(3)	109.1(12)	114.79(17)

complexes. The M−O(2) (carboxylate) and M−O(5) (water) distances are similar within a given complex [2.050(2) and 2.037(2) Å, respectively, for Co (**2**), 1.996(10) and 2.039(10) Å for Ni (**3**), and 1.9567(15) and 1.9611(16) Å for Cu (**4**)]. The M−O(1) (C=O group) distance in each case is the longest of the three independent bond lengths about the metal, because of the lesser degree of covalency for the carbonyl ligand [M−O(1) = 2.175(2), 2.094(9), and 2.3788(15) Å for **2**−**4**, respectively]. This is the bond affected by Jahn−Teller distortion in the copper complex, which has a Jahn−Teller radius of 0.48 Å.

While the intramolecular distances do not provide any surprises, the intermolecular contacts in these structures mediate the formation of a motif whose nature and symmetry are far removed from the physical shape of the molecule that forms its basic building block. Table 3 collects the shortest distances between hydrogen-bond donor (D) and acceptor (A) atoms in the crystals. As can be seen, there are a number of moderate to strong hydrogen bonds, in particular those between O(5) (ligated water) and O(6) (free water), O(5) and O(4) (oxalurate urea carbonyl), and O(6) and O(2) (oxalurate-ligated carboxylate). The N(1) (oxalurate amide) and O(3) (oxalurate pendant carboxylate) atoms of the same ligand also make a short contact that must also provide electrostatic stabilization.

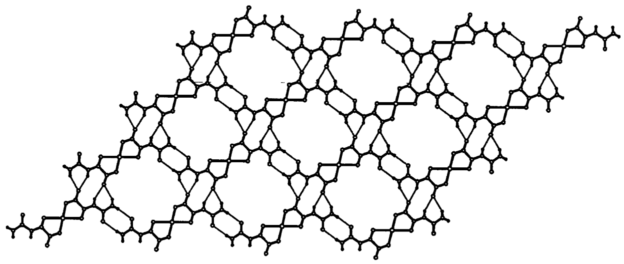

Figure 3. Drawing of the 2-D net formed by "M(oxalurate)$_2$" moieties.

Table 3. Shortest D···A Distances (Å) for $[M(oxalurate)_2(H_2O)_2]\cdot 2H_2O$ (M = Co (**2**), Ni (**3**), Cu (**4**))

	distances, Å			
D···A	Co	Ni	Cu	symmetry
N(1)···O(3)	2.880(4)	2.859(15)	2.897(2)	$x, -y - 1, -z + 1$
N(2)···O(4)	2.996(4)	2.985(16)	2.971(2)	$-x - 2, -y, -z + 1$
N(2)···O(3)	2.931(4)	2.942(16)	2.910(3)	$-x, -y - 1, -z + 1$
O(5)···O(6)	2.634(4)	2.667(14)	2.634(3)	$-x, -y + 1, -z$
O(5)···O(4)	2.713(4)	2.705(13)	2.714(2)	$x + 1, y, z$
O(5)···O(1)	3.040(4)	3.054(14)	2.907(2)	$x + 1, y, z$
O(6)···O(2)	2.676(4)	2.687(14)	2.710(2)	$x - 1, y + 1, z$
O(6)···O(5)	2.830(4)	2.815(14)	2.815(3)	
N(1)···O(3)	2.685(4)	2.672(15)	2.677(2)	

The hydrogen bonds join the coordination complexes into a nearly square two-dimensional net (Figure 3), in which parallel sides of the basic unit, a slightly distorted square, are related by a crystallographic inversion center. The core of the coordination complex resides on one crystallographically independent edge of the square, and the adjacent side is formed by a self-complementary hydrogen-bonded pair of terminal urea fragments. The two inversion-related congeners of these sides complete the basic unit of the net. Alternatively, the net can be viewed as a lattice formed by two distinct types of ribbon propagated in directions roughly perpendicular to each other, and intersecting at the corners of the squares. One of the ribbons contains the planar chelate core ("MO_4C_4") of the complex and the proximal parts of the oxalurate ligands, while the other ribbon is comprised largely of the distal urea fragments of the oxalurate ligands. From yet a different point of view, the 2-D net can also be described as ribbons formed by a complex self-assembled pattern of oxalurates bridged by the metal atoms.

The complex self-assembled ribbon formed by the oxalurate moieties can best be described with reference to Figure 4. Each oxalurate is hydrogen bonded to two others in quite different manners. The first and more complex interaction, consisting of a DDA−ADD sequence, [H(N(2A)), H(N(1A)), O(3A) to O(3), H(N(1)), H(N(2)], is a self-complementary union in which each oxygen atom acts as an acceptor for two hydrogen bonds. This unusual intermolecular junction is enabled by the conformation of the oxalurate ligand in

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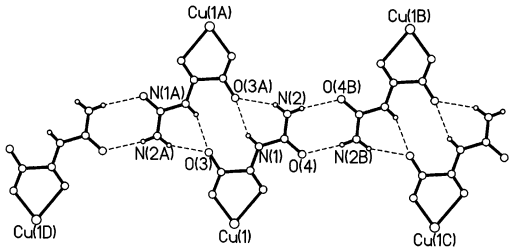
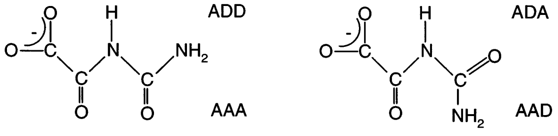


Figure 4. Drawing of the ribbon formed by the self-assembly of oxalurate groups.



(a)

(b)

Figure 5. Conformation of oxalurate: (a) in compounds **2**−**4**; (b) in other compounds.

these complexes. The oxalurate, which is planar, here possesses a conformation which situates three oxygen atoms (AAA) along the side of the ligand that is proximal to the metal atom, as in Figure 5a. This arrangement leaves C═O, NH, and NH_2 (ADD) groups on the distal side of the ligand. The two oxalurate-containing structures that have been reported previously present a different conformation in which hydrogen atoms are present on both sides of the backbone (ADA and AAD), Figure 5b.

The second intermolecular interaction involving oxalurate is of the type $R_2^2(8)$[13] [O(4), H(N(2)) and H(N(2B)), O(4B)] in Figure 4, an often observed motif for complexes containing polyfunctional ligands.

This complex, unbounded one-dimensional aggregate is cross-linked by the metal atoms to form a two-dimensional pattern which possesses a nearly square topology. Each basic, cyclic unit in which six oxalurate groups and two metal atoms are involved contains 24 atoms.

Two-dimensional networks formed by coordination complexes almost always have the metal center located at the corners of the basic motif. In contrast, the rings formed by complexes **2**−**4** have at their corners the unusual self-complementary DDA−ADD junction possessing four hydrogen bonds—a strong but flexible union exploiting the topological corner that oxalurate presents to its surroundings.

The degree of flexibility that these corners provide to the overall structure is seen in the fact that the same topology and structural type persist across this series of three complexes, even though one of them, **4**, has a significantly distorted core as a result of the Jahn−Teller effect at the copper center. This persistence of structural integrity stands in contrast to what has been observed in some other richly hydrogen-bonded molecular solids such as the copper and chromium Tutton salts, in which the slight steric perturbation produced by deuteration[14] or light doping[15] with the analogous complex of zinc is enough to cause a change of structure type.

Figure 6 shows one unit of the basic cyclic motif of the 2-D net, along with the water molecules that line it. The coordinated oxygen atoms [O(1), O(2)] of the oxalurate ligand have one acceptor site available after coordination to the metal. However, while O(2) participates in a rather strong hydrogen bond with H(O) of an unligated water molecule [D···A = 2.676(4) (**2**), 2.687(14) (**3**), and 2.710(2) (**4**) Å], the carbonyl oxygen atom O(1)—the site affected by Jahn−Teller distortion in the Cu compound and which is a poorer hydrogen-bond acceptor than the carboxylate oxygen (O(2))—presents only a weak interaction with the H(O) of a coordinated water molecule. For compound **2**, for example, the O(1)···O(5) distance is 3.040(4) Å with an O(1)···H(O(5)) distance of 2.64(5) Å and an O(1)···H−O(5) angle of 120(5)°. Inasmuch as O(1) is not strongly constrained by hydrogen bonding, it accordingly possesses the freedom necessary for adapting to the Jahn−Teller effect, a fact reflected in the significant change in the O···O nonbonded contact distance on passing from complexes **2** and **3** to **4**. This degree of freedom is independent of that granted to the ligand periphery by the flexible molecular junctions, which is also necessary to accommodate the Jahn−Teller distortion.

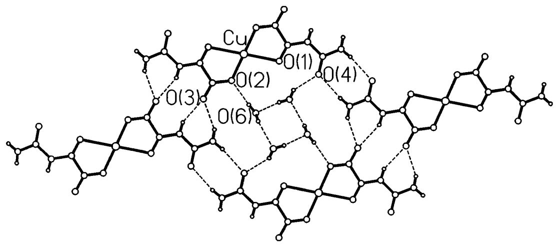


Figure 6. Drawing of a cyclic motif of the 2-D net formed by $M(oxalurate)_2$ moieties showing the hydrogen bonding with the water molecules.

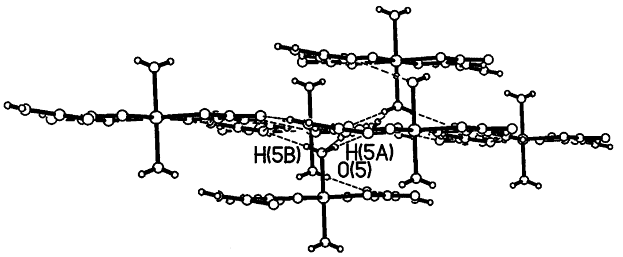


Figure 7. Side-on view of the "$Cu(oxalurate)_2$" sheets showing the interaction between the metal-bound H_2O molecules (O(5)H(5A)H(5B)) and adjacent sheets.

Of the four water molecules lining the cycle, two are water molecules of crystallization [O(6)] and the other two are axially coordinated water molecules [O(5)] from complexes in the layers immediately above and below the ring under consideration. This hydrogen-bonded link is the topological peg that binds adjacent layers into a stable three-dimensional lattice (Figure 7).

The three H atoms bonded to the N atoms of oxalurate are used in hydrogen bonds with other oxalurates (Figure 4); the amide H(N(1)) is hydrogen bonded to an equivalent

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of O(3) in the DDA−ADD interaction, as is one of the amine H(N(2)) atoms of the same ligand. The second amine H atom is donated to O(4) of a neighboring oxalurate in the eight-membered ring interaction. So, the acceptor atom O(3) receives two hydrogen bonds from an adjacent oxalurate, while O(4) is an acceptor in an interaction with an oxalurate neighbor and also accepts a hydrogen bond from a ligated water molecule, as seen in Figure 6.

Each water molecule also presents a further complement of hydrogen bonds. In addition to the (water)O−H···O-(oxalurate) contacts that hold the water moieties to the interior of the cyclic motif, the four water molecules lining a given ring are hydrogen bonded to each other to form their own cyclic pattern, thus serving as a bushing inside the larger cycles formed by the coordination complexes.

The packing pattern that these molecules present allows all of the potential hydrogen-bond donor and acceptor atoms to employ their full potential to form hydrogen bonds, except for the unligated water molecules, which possess one free acceptor site, and the coordinated amide oxygen atom, which has just one weak noncovalent contact.

The IR data for these three solids can be understood in terms of the crystal structures. Each of the complexes displays a strong IR peak at ~3550 cm^{-1} (see the Experimental Section) corresponding to the ν(OH) of the water molecules. In the range of 3400−3200 cm^{-1}, we observed the absorptions corresponding to ν(NH) of the NH and NH_2 groups of the oxalurate ligands. The absorptions corresponding to ν(CO) appear at around 1700 cm^{-1}, but it is not possible to obtain further information from these signals because of their breadth and because of the number of noncovalent interactions and types of CO groups.[16] Oxaluric acid itself displays a strong band at 1714 cm^{-1}. The same band shifts to 1745 cm^{-1} for sodium oxalurate and to 1756−1761 cm^{-1} for the coordination compounds.

There are also absorptions in the range 1650−1550 cm^{-1} attributable to the HOH bending of the water molecules or to the degenerate deformation of the NH_2 group. There is a strong absorption at 1512 cm^{-1} (**2**), 1511 cm^{-1} (**3**), and 1501 cm^{-1} (**4**) arising from the chelating coordination of the oxalurate ligand. Neither oxaluric acid nor sodium oxalurate displays this band. We observe a peak at 1110 cm^{-1} for oxaluric acid and sodium oxalurate which is not present in the IR spectra of the complexes and which can be used for determining the purity of the coordination complexes. Finally, there are absorptions in the 550−450 cm^{-1} region that correspond to the twisting and wagging modes of the aqua ligands as well as to vibrational modes of the lattice water molecules.

Conclusion

The oxalurate ligand displays a striking variety of covalent and noncovalent interactions in these three complexes, acting as a chelate ligand, and adopting a conformation that permits the formation of distinct hydrogen-bonding self-recognition patterns at intermolecular junctions. The supramolecular pattern formed possesses a nearly square topology, thus demonstrating how the latent topological symmetry in the individual molecules can be expressed in the aggregate structure. Two different kinds of chains are formed, one of them propagated through two different self-recognition patterns and the other through bridging metal atoms chelated by oxalurate ligands. The resulting 2-D motif has a unit mesh consisting of a 24-atom ring, with 22 of the atoms belonging to oxalurate groups. The 2-D nets are stacked, with axial water ligands from one layer forming hydrogen bonds to the inside of the ring motif from the next. These water moieties and unligated waters assemble into a cyclic hydrogen-bonded pattern, thus forming a bushing around the inside of the larger ring. The solid-state structure of these complexes demonstrates the versatility and part of the larger potential that oxalurate possesses for use in coordination and supramolecular chemistry.

Experimental Section

Instrumentation. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer 240-B or 2400 microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (4000−200 cm^{-1}) from Nujol mulls between polyethylene sheets.

Synthesis of $NaCO_2CONHCONH_2$ (1). A 7.5 mL sample of a NaOH solution (1.014 mol/L, 7.605 mmol) was added to a water suspension of oxaluric acid, $HOOCCONHCONH_2$ (1.000 g, 7.57 mmol/15 mL). The NaOH addition produced a partial solubilization of the acid and then the precipitation of a white solid. After 15 min of stirring, the solid was filtered off, washed with *i*-PrOH, and characterized as $NaCO_2CONHCONH_2$ (**1**) (1.00 g, 86% yield).

Anal. Calcd for $NaC_3O_4N_2H_3$ (MW 154): C, 23.37; H, 1.94; N, 18.18. Found: C, 23.28; H, 1.48; N, 17.94. IR (ν, cm^{-1}): 3401 (s, ν(OH)), 3277 and 3210 (s, ν(NH)), 1745 (s, ν(CO)), 1673 (m, ν(CO)), 1603 (m), 1183 (m), 1114 (m), 785 (s), 605 (s), 590 (s), 327 (m).

Synthesis of *trans*-[Co(oxalurate)$_2$(H_2O)$_2$]·2H_2O (2). $Co(NO_3)_2$·6H_2O (0.075 g, 0.26 mmol) was added to an aqueous sodium oxalurate solution (0.080 g, 0.52 mmol/10 mL of water). The solution was stirred for 90 min, and the resulting solid was filtered off, washed with *i*-PrOH, and characterized as *trans*-[Co(oxalurate)$_2$(H_2O)$_2$]·2H_2O (**2**) (0.055 g, 54% yield).

Anal. Calcd for $CoC_6O_{12}N_4H_{14}$ (MW 393.1): C, 18.32; H, 3.56; N, 14.25. Found: C, 18.31; H, 3.02; N, 13.83. IR (ν, cm^{-1}): 3541 (s, ν(OH)), 3383 and 3242 (s, ν(NH)), 1757 (s, ν(CO)) 1680 with one shoulder (s, ν(CO)), 1512 (s), 1231 (s), 764 (m), 638 (m), 586 (s), 562 (s), 504 (m), 453 (m), 313 (m).

Synthesis of *trans*-[Ni(oxalurate)$_2$(H_2O)$_2$]·2H_2O (3). $Ni(NO_3)_2$·6H_2O (0.094 g, 0.32 mmol) was added to an aqueous sodium oxalurate solution (0.100 g, 0.65 mmol/8 mL of water). The solution was stirred for 10 min, and 40 mL of *i*-PrOH was added. The mixture was stored at 4 °C for 24 h, and the resulting solid, *trans*-[Ni(oxalurate)$_2$(H_2O)$_2$]·2H_2O (**3**), was filtered off and washed with water (0.050 g, 39% yield).

Anal. Calcd for $NiC_6O_{12}N_4H_{14}$ (MW 392.9): C, 18.32; H, 3.56; N, 14.25. Found: C, 17.60; H, 3.42; N, 13.54. IR (ν, cm^{-1}): 3541 (s, ν(OH)), 3383 and 3242 (s, ν(NH)), 1761(s, ν(CO)) 1689 with one shoulder (s, ν(CO)), 1511 (s), 1234 (s), 764 (m), 638 (m), 586 (s), 563 (s), 503 (m), 457 (m), 328 (m).

Synthesis of *trans*-[Cu(oxalurate)$_2$(H_2O)$_2$]·2H_2O (4). $CuCl_2$·2H_2O (0.055 g, 0.33 mmol) was added to an aqueous sodium oxalurate solution (0.100 g, 0.65 mmol). The mixture was stirred

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(16) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227−250.

for 5 min, and the blue solid precipitate was filtered off, washed with *i*-PrOH, and characterized as *trans*-[Cu(oxalurate)$_2$(H$_2$O)$_2$]·2H$_2$O (**4**) (0.11 g, 80% yield).

Anal. Calcd for $CuC_6O_{12}N_4H_{14}$ (MW 397.75): C, 18.11; H, 3.52; N, 14.08. Found: C, 17.94; H, 3.30; N, 13.78. IR (ν, cm^{-1}): 3551 (s, ν(OH)), 3377 and 3271 (s, ν(NH)), 1756 (s, ν(CO)) 1674 with two shoulders (s, ν(CO)), 1501 (s), 1218 (s), 759 (m), 638 (m), 585 (s), 575 (s), 503 (m), 475 (m), 451 (m), 323 (m).

X-ray Structure Determination. Suitable single crystals of **2** and **4** for X-ray diffraction were obtained in each case by slow evaporation of a water solution of parabanic acid, NaOH, and MCl_2 (2:2:1 ratio). Single crystals of compound **3** were obtained by slow diffusion of a water solution of sodium oxalurate into a solution of $Ni(NO_3)_2$ in methanol through a layer of 2-methyl-2,4-pentanediol.

A Nonius CAD-4 diffractometer was used for data collection for the three compounds. After data reduction and application of absorption corrections the structures were solved by direct methods and were refined by full-matrix least-squares.[17] The hydrogen atoms of compounds **2** and **4** were located in difference Fourier maps and were refined as independent atoms. No hydrogen atoms were located for compound **3**, which was a poorly diffracting crystal probably due to its size (0.12 × 0.07 × 0.06 mm). The refinements converged with the residuals given in Table 1.

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Supporting Information Available: Crystallographic data for compounds **2**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Diffractometer control program: CAD4/PC Version 2.0, Nonius bv, Delft, The Netherlands, 1996. (b) Data were processed on an AlphaStation 200 4/166 (OpenVMS/Alpha V6.2), with the program XCAD4B (K. Harms, 1996) and with the commercial package SHELXTL Rel. 5.05/VMS, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996. (c) Direct methods: SHELXS-97: Fortran program for crystal structure solution, George M. Sheldrick, 1997. (d) Refinement: SHELXL-97: Fortran program for crystal structure refinement, George M. Sheldrick, 1997.