Synthesis and Structural Studies of Metal Complexes of the Biological Ligand 2-Quinaldic Acid: Utilization of the Polymer Pendant Analog PS-2-QA for Selective Aluminum Ion Removal from Aqueous Solution

Wei Li,[1a] Marilyn M. Olmstead,[1b] Dana Miggins,[1a,c] and Richard H. Fish*,[1a]

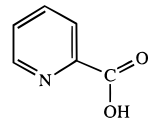
Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, and Department of Chemistry, University of California, Davis, California 95616

Received April 26, 1995[⊗]

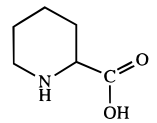
The synthetic reactions of quinaldic acid (**2-QA, 1**), a ligand with potential implications in Al^{3+} ion biological transport and in pharmaceutical applications and of use for the removal and recovery of Al^{3+} ions from environmental waste sites, were studied with tri- and divalent metal ions that encompass Al^{3+}, Fe^{3+}, Ga^{3+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}. The Al^{3+}, Fe^{3+}, and Ga^{3+} metal ion complexes, **2**−**4**, of **1** were characterized by FT-IR, FAB/MS, NMR, and elemental analysis and provided the following structural formula with **1** of **2-QA**$_4$M$_2$(μ-OH)$_2$·S, where S = H_2O or pyridine. In the case of the Ga^{3+} analog, **4**·Py, the unequivocal μ-OH dimer structure was determined by single-crystal X-ray analysis [space group, *P*1; a = 13.387(3) Å; b = 14.016(2) Å; c = 14.549(2) Å; α = 87.74(2)°; β = 73.44(2)°; γ = 82.61(2)°; Z = 2; volume = 2592.6 Å^3]. A description of the X-ray crystal structure of **2-QA**$_4$Ga$_2$(μ-OH)$_2$·4 pyridine, **4**·Py, will also be presented. The corresponding bis(**2-QA**) metal complexes of Zn^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}, **5**−**8**, were also studied and all provided a formula of **2-QA**$_2$M·1.5 H_2O, which were also characterized by many of the above-mentioned spectroscopic techniques. The polymer-supported (**PS**) version of **1**, **PS-2-QA**, bonded to modified, macroporous 6% cross-linked polystyrene−divinylbenzene beads, was synthesized by an electrophilic substitution reaction on the aromatic ring of a **2-QA** derivative, ethyl 2-quinaldate, with the chloromethylated precursor, **PS-CH$_2$Cl**, followed by subsequent ester hydroysis to the free **PS-2-QA** ligand. The **PS-2-QA** ligand was found to selectively remove Al^{3+} ions from aqueous acidic solution (pH = 3−5) in the presence of other divalent metal ions, namely, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+} as well as a trivalent metal ion, Cr^{3+}.

Introduction

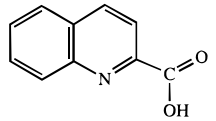
There has been a significant new focus on the aluminum ion (Al^{3+}) because of its role as a neurotoxic agent in the environment and the more insidious accumulation of this metal ion in man.[2] Therefore, the importance of Al^{3+} ions in biological systems has attracted great interest in the study of its coordination chemistry with ligands thought to play a biological role in these processes.[3] For example, picolinic acid, **2-PA**, a tryptophan metabolite, and pipecolinic acid, **2-PIP**, are two of the ligands that were studied because of their biological connections with the Al^{3+} ion.[4] It is interesting to note that the structural studies that were reported for the Al^{3+} ion complexes containing these biological ligands, **2-PA** and **2-PIP**, as a function of the pH of the solution were carried out by ^{1}H NMR, IR, and thermogravimetric techniques followed by isolation and elemental analysis.[4] For example, a variety of Al^{3+} complexes were noted with the biological ligand **2-PA** and ranged from [Al(**2-PA**)]$^{2+}$, [Al(**2-PA**)$_2$]$^+$, and [Al(**2-PA**)OH] to Al(**2-PA**)$_3$, *all mononuclear*.



2-PA



2-PIP



2-QA, 1

Thus, we decided to study the coordination chemistry of a ligand structurally similar to **2-PA**, 2-quinaldic acid, **2-QA**, ligand **1**, which itself has been associated with tryptophan metabolism[5] and, therefore, would be a potential biological Al^{3+} ion transport ligand, as well as having been shown to have pharmaceutical applications.[6] Moreover, **2-QA** has important potential applications in the removal and recovery of Al^{3+} ions from acidic environmental waste sites, an application that is of prime importance because of the role of Al^{3+} ions as a neurotoxic comtaminant and its economic value.

A perusal of the literature verified that only the Cu^{2+} and Rh^+ complexes of **1** had been structurally characterized.[7a,b] The X-ray study of the Cu^{2+} complex of **1** demonstrated that it is a

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) (a) University of California, Berkeley. (b) University of California, Davis. (c) DOE Science and Education Semester Fellowship (Jackson State University, Jackson, MS).

(2) Martin, R. B. *Acc. Chem. Res.* **1994**, *27*, 204, and references therein.

(3) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons, Inc: New York, 1988; p 216. (b) Martin, R. B. In *Bioinorganic Chemistry of Aluminum*; Siegel H., Siegel A., Eds.; Aluminum and Its Role in Biology, Metal Ions in Biological Systems, Vol. 24; Marcel Dekker: New York, 1988; 1, and references therein. (c) Robinson, G. H., Ed. *Coordination Chemistry of Aluminum*; VCH Publishers, Inc.: New York, 1993.

(4) Feng, T. L.; Tsangaris, J. M.; Barron, A. R. *Monatsh. Chem.* **1990**, *121*, 113.

(5) Zhou, P.; O'Hagan, D.; Mocek, U.; Zeng, Z.; Yuen, L.-D.; Frenzel, T.; Unkefer, C. J.; Beale, J. M.; Floss, H. G. *J. Am. Chem. Soc.* **1989**, *111*, 7274.

(6) (a) Kyowa Fermentation Industry Co. Ltd. Fr. Demande FR 2181563, 1974. (b) Miyata, S.; Takata, M.; Okada, A. Ger. Offen. DE 2222473 731122, 1973.

0020-1669/96/1335-0051$12.00/0 © 1996 American Chemical Society

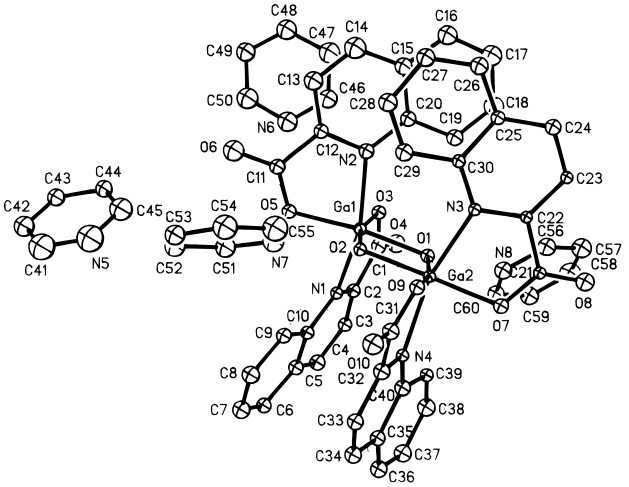


Figure 1. Thermal ellipsoid drawing of **2-QA**$_4$Ga$_2$(μ-OH)$_2$·4Py, **4·Py**.

neutral, intermediate trigonal bipyramidal/rectangular bipyramidal complex with a Cu(**2-QA**)$_2$·H$_2$O formula.[7a] Syntheses of **2-QA** complexes with lanthanides were also reported by Seninara et al.,[8] while the structures of these lanthanide complexes were thought to have a L$_3$M formula by elemental analysis and FT-IR spectroscopy; no X-ray crystallographic studies were available to confirm the proposed structures. Interestingly, it was quite surprising to find that no complexes of **1** with the Al^{3+} ion have been synthesized or structurally characterized even though this ligand has similarities to ligands, **2-PA** and **2-PIP**, that have biological significance and that may be implicated in Alzheimer's disease as biological transport agents of Al^{3+} ions.[2]

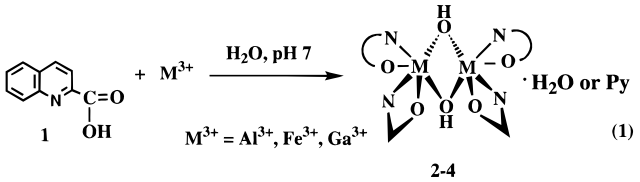
Therefore, we report on the synthesis and spectroscopic characterizations of a number of metal complexes that include the trivalent metal ions, Al^{3+}, Fe^{3+}, and Ga^{3+}, and the divalent metal ions of Zn^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}. In addition, an X-ray crystallographic analysis of the Ga^{3+} complex with **1** will be presented, which itself might have an important future application as an imaging agent.[9]

More recently, we have focused on the new area of environmental inorganic chemistry with regard to anchoring a number of organic ligands that are biomimics of known biological ligands to chemically modified, macroporous polystyrene−divinylbenzene beads for the selective removal and recovery of metal ions from aqueous acidic solution at pH values of 3 and 5.[10] Thus, we will also report on the synthesis of the polymer pendant ligand version of **1**, **PS-2-QA**, chemically bonded on a macroporous 6% polystyrene−divinylbenzene bead, and demonstrate selective Al^{3+} ion removal and recovery from aqueous acidic solution in the presence of competing tri- and divalent metal ions.

Results

Synthesis and Spectroscopic Properties of the Metal Complexes of 2-QA, 1. Trivalent Aluminum, Iron, and Gallium Ions. Since the Al^{3+} ion is of paramount importance as a potential neurotoxic product in the environment and to man, we studied it first with ligand **1**. There were no apparent changes observed when a solution of $Al(NO_3)_3$ was added to a solution of **1** in water without any pH manipulations. However, a white complex, **2**, precipitated out of solution when the pH was raised to ∼7.0. A spectroscopic study that included FT-IR [(C═O, cm^{-1}: 1682 (br, s), 1374 (s), 1342 (s)],[8] fast atom bombardment mass spectrometry (FAB/MS) [(*m/z* (%)): 759 **2-QA**$_4$Al$_2$(OH)$^+$ (80), 587 [**2-QA**$_3$Al$_2$(O)]$^+$ (78), 371 **2-QA**$_2$-Al$^+$ (70)], and ^{1}H NMR [(DMSO-d_6, TMS, δ): 8.16 (doublet, J = 4 Hz, 1H), 7.92 (multiplet, J = 4 Hz, 2H), 7.40 (doublet, J = 4 Hz, 1H), 7.12 (triplet, J = 4 Hz, 1H), 6.82 (triplet, J = 4 Hz, 1H)] and ^{27}Al NMR [(DMSO-d_6/H$_2$O, Al(H$_2$O)$_6^{3+}$, δ): 10 ppm (550 Hz bw)], in conjunction with elemental analysis, provided the formula, **2-QA**$_4$Al$_2$(μ-OH)$_2$·3 H$_2$O, for complex **2**.

Similarly, the Fe^{3+} and Ga^{3+} analogs, **3** and **4**, were prepared from reactions of $Fe(NO_3)_3$ or $Ga(NO_3)_3$ with **1** at pH 7 to provide the μ-hydroxy dimer structures as illustrated in eq 1. Complexes **3** and **4** were judged to be isostructural with **2** based on similar FAB/MS, IR, NMR, and elemental analysis data (see the Experimental Section).



(1)

Table 1. Data for the Crystal Structure Analysis of **4·**Py

compound	**4·**Py
formula	$C_{60}H_{46}Ga_2N_8O_{10}$
a, Å	13.387(3)
b, Å	14.016(2)
c, Å	14.549(2)
α, deg	87.74(2)
β, deg	73.44(2)
γ, deg	82.61(2)
Z	2
V, Å^3	2592.6
space group	*P*1
D_{calc}, g/cm^3	1510
crystal size, mm	0.05 × 0.13 × 0.13
$2q_{max}$, deg	114
temp, K	130
no. of reflns collected	7011
no. of reflns used ($F_o > 6\sigma(F_o)$)	3174
abs correction	XABS[a]
no. of variables	331
final R/R_w, %	6.43/5.89

[a]Program XABS provides an empirical correction based on F_o and F_c differences (Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis).

X-ray Crystal Structure of Complex 4·Py. We were able to obtain the single-crystal X-ray crystallographic structure of the Ga^{3+} analog, **4·Py**, a neutral complex with four pyridine molecules associated with the unit cell, to provide unequivocal evidence for the μ-hydroxy dimer core for the trivalent metal ion complexes of **1**. A thermal ellipsoid drawing of **4·Py** is shown in Figure 1, while relevant crystal data are given in Table 1, and Table 2 provides important bond length and angle data.

The two Ga^{3+} centers are identical, with both bound to two ligands via N,O-coordination, which features octahedral coordination. The Ga−O (OH) bond distances, averaging 1.933(8) Å, are comparable to the typical Ga−O bond distances found in other Ga^{3+} μ-hydroxy complexes.[11] However, they are slightly shorter than the Ga−O (CO_3^{2-}) bond distances (1.949(8) Å). Both Ga−O bond distances (1.949(8) Å) and Ga−N bond

(7) (a) Haendler, H. M. *Acta. Crystallogr.* **1986**, *C42*, 147. (b) Lamprecht, G. J.; Beetge, J. H.; Leipoldt, J. G.; De Waal, D. R. *Inorg. Chim. Acta.* **1986**, *113*, 157.
(8) Seminara, A.; Musumeci, A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 599.
(9) Bollinger, J. E.; Mague, J. T; Roundhill, D. M. *Inorg. Chem.* **1994**, *33*, 1241.
(10) (a) Huang, S.-P.; Li, W.; Franz, K. J.; Albright, R. L.; Fish, R. H. *Inorg. Chem.* **1995**, *34*, 2813. (b) Huang, S.-P.; Franz, K. J.; Olmstead, M. M.; Fish, R. H. *Inorg. Chem.* **1995**, *34*, 2820.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $L_4Ga_2(OH)_2$, **4·Py**

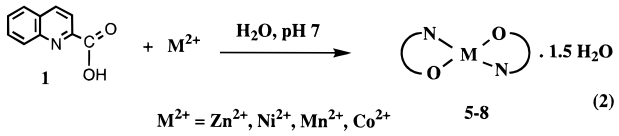
Bond Distances			
Ga(1)−O(1)	1.945(8)	Ga(1)−O(2)	1.928(8)
Ga(1)−O(3)	1.935(8)	Ga(1)−O(5)	1.949(8)
Ga(1)−N(1)	2.132(8)	Ga(1)−N(2)	2.124(9)
Ga(2)−O(1)	1.945(8)	Ga(2)−O(2)	1.913(7)
Ga(2)−O(7)	1.955(8)	Ga(2)−O(9)	1.956(8)
Ga(2)−N(3)	2.113(8)	Ga(2)−N(4)	2.125(9)
O(3)−C(1)	1.297(12)	O(4)−C(1)	1.205(16)
O(5)−C(11)	1.293(13)	O(6)−C(11)	1.231(16)
O(7)−C(21)	1.290(14)	O(8)−C(21)	1.226(15)
O(9)−C(31)	1.285(15)	O(10)−C(31)	1.228(16)
N(1)−C(2)	1.319(15)	N(1)−C(10)	1.388(16)
N(2)−C(12)	1.333(16)	N(2)−C(20)	1.401(16)
N(3)−C(22)	1.329(15)	N(3)−C(30)	1.370(13)
N(4)−C(32)	1.311(17)	N(4)−C(40)	1.379(13)
H(1)···N(8)	1.93(2)	H(2)···N(7)	1.83(2)
Bond Angles			
O(1)−Ga(1)−O(2)	74.2(3)	O(1)−Ga(1)−O(3)	90.6(3)
O(2)−Ga(1)−O(3)	164.3(3)	O(1)−Ga(1)−O(5)	164.7(4)
O(2)−Ga(1)−O(5)	90.9(3)	O(3)−Ga(1)−O(5)	104.5(3)
O(1)−Ga(1)−N(1)	94.2(3)	O(2)−Ga(1)−N(1)	104.2(3)
O(3)−Ga(1)−N(1)	80.3(3)	O(5)−Ga(1)−N(1)	86.1(3)
O(1)−Ga(1)−N(2)	103.5(3)	O(2)−Ga(1)−N(2)	94.1(3)
O(3)−Ga(1)−N(2)	85.6(3)	O(5)−Ga(1)−N(2)	80.5(4)
N(1)−Ga(1)−N(2)	157.5(3)	O(1)−Ga(2)−O(2)	74.5(3)
O(1)−Ga(2)−O(7)	92.1(3)	O(2)−Ga(2)−O(7)	165.8(3)
O(1)−Ga(2)−O(9)	166.6(3)	O(2)−Ga(2)−O(9)	93.0(3)
O(7)−Ga(2)−O(9)	100.8(3)	O(1)−Ga(2)−N(3)	93.3(3)
O(2)−Ga(2)−N(3)	104.4(3)	O(7)−Ga(2)−N(3)	80.6(3)
O(9)−Ga(2)−N(3)	85.0(3)	O(1)−Ga(2)−N(4)	104.8(3)
O(2)−G(2)−N(4)	92.3(3)	O(7)−Ga(2)−N(4)	86.6(3)
O(9)−Ga(2)−N(4)	80.1(3)	N(3)−Ga(2)−N(4)	158.2(3)
Ga(1)−O(1)−Ga(2)	104.7(4)	Ga(1)−O(2)−Ga(2)	106.6(4)
O(1)−H(1)···N(8)	176(2)	O(2)−H(2)···N(7)	167(2)

distances (2.123(8) Å) between Ga and **2-QA** ligands are slightly longer than those found in a Ga^{3+} complex of a hexachelating ligand, 1,4,7-triazacyclononane-1,4,7-triacetic acid (1.930(2) Å for Ga−O and 2.090(3) Å for Ga−N, respectively).[12] Two of the four pyridine molecules are associated with the Ga^{3+} complex, **4·Py**, via hydrogen bonding, N···H−O, with hydrogen bonding distances between the N atom on the pyridine and the μ-hydroxy group, N···H, averaging 1.88(2) Å.

The quinoline ring and the five-membered ring formed via the N,O-coordination with Ga^{3+} are almost in the same plane, which minimizes any steric effects. This is shown by the following bond angles: C32−N4−C40 = 119.9(10)°; Ga2−N4−C32 = 111.4 (7)°; Ga2−N4−C40 = 128.7(8)°. As a result, the two planes associated with the two ligands bound to the same Ga metal center are almost orthogonal to each other. Meanwhile, the two Ga^{3+} metal centers and the two oxygen atoms from the two μ-hydroxy groups are in the same plane and perpendicular to the two five-membered rings formed from the Ga^{3+} metal center and the **2-QA** ligands. It should be noted that the steric effects are minimized as the plane containing Ga(1), N(2), C(11), and O(5) parallels the plane containing Ga(2), N(3), C(21), and O(7), while the plane containing Ga(1), N(1), C(2), and O(3) parallels the plane containing Ga(2), N(4), C(31), and O(9).

It is also interesting to point out that the ^{1}H NMR spectra of the aqua complexes of **2** and **4** in DMSO-d_6 showed *upfield* chemical shifts for all the ring hydrogens of the complexed **2-QA** ligand in comparison to those of the free ligand. This signifies that there is a diamagnetic anisotropic effect of the parallel **2-QA** ligands in each plane (Figure 1) that causes these upfield shifts (0.5−0.8 ppm) to occur in solution.

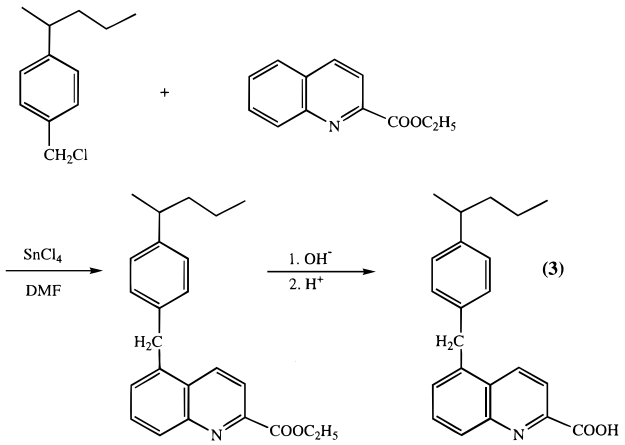
Divalent Zinc, Nickel, Manganese, and Cobalt Ions. The synthesis of the divalent analogs of ligand **1** were accomplished in a similar fashion at pH 7 (eq 2). The bis(**2-QA**) zinc



complex, **5**, was obtained as a white solid, while the Ni^{2+}, Mn^{2+}, and Co^{2+} complexes, **6**−**8**, were obtained as light-green, pale-orange, and pink solids, respectively, and were all formulated as hydrates with 1.5 molecules of H_2O based on their elemental analysis. Fortunately, their FAB/MS spectra all showed protonated molecular ions $[\mathbf{2\text{-}QA}_2M + H]^+$, while the ^{1}H NMR or UV−vis spectra were not determined because of either paramagnetism or the poor solubility of the complexes in various solvents.

The FT-IR spectra of these divalent metal aqua complexes, **5**−**8**, of **1** all show the antisymmetric and symmetric C═O stretching frequencies at 1650−1614 and 1340−1380 cm^{-1}, respectively, and were all shifted to higher frequencies when compared to **1**. Nitrogen donation from the ligand to the metal center is suggested as the cause of this shift based on an observation that these shifts are comparable to those for metal complexes of heterocyclic N-donor ligands.[8] It is interesting that the C═O shifts for the μ-hydroxy dimer complexes, **2**−**4**, were greater than those for complexes, **5**−**8**.

Synthesis of the Polymer-Supported 2-Quinaldic Acid, PS-2-QA. The corresponding polymer-supported version of **1**, anchored on modified, macroporous 6% cross-linked polystyrene−divinylbenzene beads, was synthesized to ascertain its ability to selectively remove Al^{3+} ions from aqueous acidic solution in the presence of a trivalent metal ion and a variety of divalent metal ions. The synthesis entailed electrophilic substitution on the aromatic ring of the ethyl ester of **1**, ethyl 2-quinaldate, with a **PS-CH$_2$Cl** derivative (the FT-IR spectrum of **PS-ethyl 2-QA** showed a C═O absorbance at 1720 cm^{-1}, similar to that of ethyl 2-quinaldate), followed by subsequent hydrolysis of the ester to the free acid as shown in eq 3. Among the different



solvents tried in the synthesis of **PS-2-QA**, DMF provided the highest yield of this ligand on the bead (0.6 mmol/g).

Metal selectivity experiments were conducted with the thought that the **PS-2-QA** ligand would show high selectivity to Al^{3+} ions in the presence of a variety of divalent metal ions

(11) (a) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Organometallics* **1993**, *12*, 24. (b) Hoard, J. L.; Smith, G. S. *J. Am. Chem. Soc.* **1959**, *81*, 3907.

(12) Moore, D. A.; Fanwick, P. E.; Welch, M. J. *Inorg. Chem.* **1990**, *29*, 672.

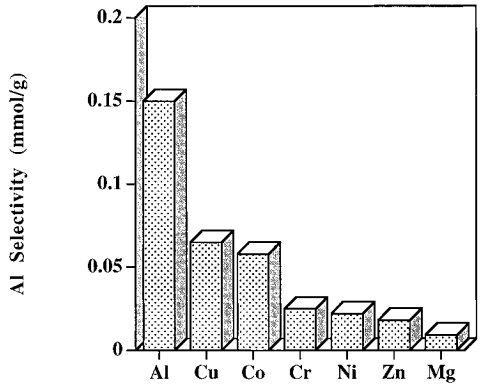


Figure 2. Selectivity of the **PS-2-QA** polymer pendant ligand to Al^{3+} at pH 3.0 in competition with other metal ions.

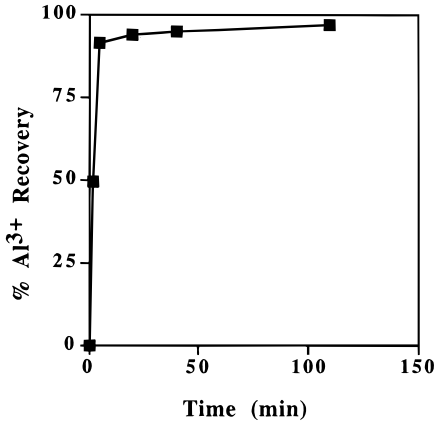


Figure 3. Rate of Al^{3+} ion recovery (%) from the **PS-2-QA**-Al^{3+} beads with 1 M H_2SO_4.

and Cr^{3+} ion at an acidic pH value of 3, and this is demonstrated in Figure 2. Indeed, Al^{3+} ions were selectively removed from solution at pH 3 in competition with Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Cr^{3+} ions. It is interesting to report that **PS-2-QA** was found to be highly selective to Fe^{3+} when Al^{3+} competes with Fe^{3+}, while Al^{3+} ions did maintain their selectivity over Cr^{3+}. Finally, the **PS-2-QA** selectivity to Al^{3+} ions did not show any improvement when the pH of the solution was raised to 5; precipitation problems occurred in the competition experiments if the pH was greater than 5.

Figure 3 shows that the complexed Al^{3+} ions on the **PS-2-QA** beads can be easily recovered in a convienent time frame by treatment with 1 M H_2SO_4. Thus, removal and recovery of the Al^{3+} ions can be achieved in a facile manner for potential future environmental applications.

Discussion

The focus of this study was a combination of the coordination chemistry of a biological ligand, **2-QA**, with trivalent and divalent metal ions and the utilization of a polymer pendant ligand version, **PS-2-QA**, for selective removal and recovery of Al^{3+} ions from aqueous acidic solutions. The use of **2-QA**, for Al^{3+} ion complexation, provided insight into the structure of a water insoluble μ-hydroxy dimer, **2**. In a previous study of the **2-PA** biological ligand, an Al^{3+} complex of the formula (**2-PA**)$_2$Al(OH) was isolated at pH 4 and was suggested to be a monomeric complex from various spectroscopic and analytical data.[4] However, no mass spectral or X-ray structural data were provided to corroborate this assignment, and from our present Al^{3+} ion results with **2-QA**, this complex might be better formulated as a μ-hydroxy dimer, **2-PA**$_4$Al$_2$(μ-OH)$_2$. It is interesting to speculate that the mononuclear complex, (**2-PA**)$_2$Al(OH), exists in solution but precipitates as a dimer at pH 4−5. Since this dimerization reaction would be concentration dependent and the ligand **2-PA** is structurally similar to **2-QA**, then this hypothesis appears reasonable.

The μ-hydroxy core structure for the trivalent metal ions, Al^{3+}, Fe^{3+}, and Ga^{3+}, was unequivocally established by FAB/MS, IR, NMR, elemental analysis, and with the single-crystal X-ray analysis of the Ga^{3+} complex, **4·Py**. Also, several divalent metal ions, Zn^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}, were reacted with **2-QA** and found to provide the bis(**2-QA**) complexes, (**2-QA**)$_2$M·1.5H_2O, as was found for the Cu^{2+} analog.[7a]

The synthesis of the polymer-supported ligand version, **PS-2-QA**, provided a venue to test the selective removal of Al^{3+} ions from aqueous acidic solutions. Although Figure 2 shows this Al^{3+} ion selectivity in the presence of various divalent ions at pH 3.0, the kinetics of this process was slow conceivably because of diffusional effects in the gel/macroporous phases. Therefore, we are in the process of attempting to selectively sulfonate the benzo ring of the **PS-2-QA** ligand, to increase the hydrophilicty of the polymer-supported ligand, in order to overcome this limiting kinetic parameter.[10]

Conclusion

Tri- and divalent metal complexes of **2-QA** were synthesized and characterized by various spectroscopic methods and by elemental analysis. The X-ray crystal structure of **4·Py** was determined, and the data showed an octahedral Ga^{3+} complex formed by N,O-chelation with two of the bidentate **2-QA** ligands surrounding a μ-hydroxy dimer core. Complex **4·Py** is, to our knowledge, the first structurally characterized example of an octahedral Ga^{3+}-**2-QA** complex. The reported homogeneous chemistry concerning the spectroscopic and structural properties of these **2-QA** metal complexes is part of our continuing investigations to understand similar polymer pendant ligand chemistry in order to design metal ion selective, polymer-supported ligands of biological relevance for removal and recovery of environmental and economic metal ions from aqueous waste sites.[10]

Experimental Section

Chemicals and Instrumentation. The 2-quinaldic acid monohydrate, $Ga(NO_3)_3{\cdot}H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$, $MnCl_2{\cdot}4H_2O$, and $Co(NO_3)_2{\cdot}6H_2O$ were purchased from Aldrich and used without further purification. Ethyl 2-quinaldate was prepared using a procedure recommended by Vogel[13] for a similar preparation of ethyl nicotinate. The FT-IR spectra were determined for the samples as solids in a KBr matrix in the mid-IR region (400−4000 cm^{-1}) using a computer-controlled Nicolet Impact 400 FT-IR spectrometer. Microanalysis and FAB/MS spectra were performed by the microanalysis and mass spectrometry laboratories located in the Department of Chemistry, University of California, Berkeley. The ^1H NMR spectra (δ in ppm relative to TMS) were recorded on a Bruker AM-500 spectrometer and the ^{27}Al NMR spectra for **2** was provided by Dr. Andrew Barron, Rice University, and was obtained on a Bruker WM 300 (δ in ppm relative to $Al(H_2O)_6^{3+}$).

Synthesis of Complex 2·3H_2O. Quinaldic acid monohydrate (300 mg, 1.73 mmol) was dissolved in H_2O (40 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Al(NO_3)_3{\cdot}9H_2O$ (325 mg, 0.88 mmol) of H_2O (10 mL) was added with stirring to the above solution, providing a white precipitate, complex **2**, which started to form immediately. After ∼1 h, the precipitate was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to give **2** in 70% yield. ^1H NMR (DMSO-d_6, δ): 8.16 (doublet, J = 4 Hz, 1H); 7.92 (multiplet, J = 4 Hz, 2H), 7.40 (doublet, J = 4 Hz, 1H), 7.12 (triplet, J = 4 Hz, 1H), 6.82 (triplet, J = 4 Hz,

(13) Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Longman: London, 1972; p 177.

1H). ^{27}Al [DMSO-d_6/H_2O, $Al(H_2O)_6^{3+}$, δ]: 10 ppm (550 Hz bw). For comparison the ^{1}H NMR (DMSO-d_6) of **1** provides the following data (δ): 8.51 (doublet, J = 4 Hz, 1H), 8.12 (multiplet, J = 4 Hz, 2H), 8.04 (doublet, J = 4 Hz, 1H), 7.83 (triplet, J = 4 Hz, 1H), 7.70 (triplet, J = 4 Hz, 1H). FT-IR (KBr, C═O, cm^{-1}): 1682 (br, s), 1374 (s), 1342 (s). FAB/MS (m/z (%)): 759 $[QA_4Al_2(OH)]^+$ (80), 587 $[QA_3Al_2(O)]^+$ (78), 371 QA_2Al^+ (70). Anal. Calcd (found) for $C_{40}H_{32}N_4O_{13}Al_2$: C, 57.84 (58.23); H, 3.88 (4.08); N, 6.74 (7.09).

Synthesis of Complex 3·3H$_2$O. Quinaldic acid monohydrate (300 mg, 1.73 mmol) was dissolved in H_2O (40 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Fe(NO_3)_2$·9H_2O (353 mg, 0.88 mmol) in H_2O (10 mL) was added, and a bright-orange precipitate of **3** started to form immediately. After 30 min, the precipitate was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to provide a 75% yield. FT-IR (KBr, C═O, cm^{-1}): 1661 (sh, s), 1332 (sh, s). FAB/MS (m/z (%)): 645 $[QA_3Fe_2(O)]^+$ (26), 401 QA_2Fe^+ (28). Anal. Calcd (found) for $C_{40}H_{28}N_4O_{11}Fe_2$: C, 56.36 (56.44); H, 3.31 (3.75); N, 6.57 (6.72).

Synthesis of Complex 4·3H$_2$O. Quinaldic acid monohydrate (200 mg, 1.15 mmol) was dissolved in H_2O (30 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Ga(NO_3)_3$·H_2O (148 mg, 0.58 mmol) in H_2O (10 mL) was added to the above solution with stirring, and a white precipitate of **4** started to form immediately. After 15 min, the precipitate was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to give a 78% yield. ^{1}H NMR (DMSO-d_6, δ): 8.23 (doublet, J = 4 Hz, 1H), 8.05 (multiplet, J = 4 Hz, 2H), 7.45 (doublet, J = 4 Hz, 1H), 7.15 (triplet, J = 4 Hz, 1H), 6.80 (triplet, J = 4 Hz, 1H). FT-IR (KBr, C═O, cm^{-1}): 1673 (br, s), 1371 (s), 1336 (s). FAB/MS (m/z (%)): 413 QA_2Ga^+ (66). Anal. Calcd (found) for $C_{40}H_{28}N_4O_{11}Ga_2$: C, 54.59 (54.12); H, 3.21 (3.62); N, 6.36 (6.61). Single crystals of **4·Py** that were suitable for X-ray crystallographic studies were grown from a pyridine/ether mixture at ambient temperature. Therefore, the three H_2O molecules of hydration are replaced by four pyridine molecules.

Synthesis of Complex 5·1.5H$_2$O. Quinaldic acid monohydrate (200 mg, 1.15 mmol) was dissolved in H_2O (30 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Zn(NO_3)_2$·6H_2O (172 mg, 0.58 mmol) in H_2O (10 mL) was added to the above solution, and a white precipitate started to form immediately. After ~$^1/_2$ h, the precipitate of **5** was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to provide a 77% yield. FT-IR (KBr, C═O, cm^{-1}): 1650 (sh), 1633 (br, s), 1391 (s), 1378 (sh), 1348 (s). FAB/MS (m/z (%)): 409 $[QA_2Zn+H]^+$ (58). Anal. Calcd (found) for $C_{20}H_{14}N_2O_5Zn$: C, 56.16 (56.53); H, 3.30 (3.69); N, 6.55 (6.91).

Synthesis of Complex 6·1.5H$_2$O. Quinaldic acid monohydrate (200 mg, 1.15 mmol) was dissolved in H_2O (30 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Ni(NO_3)_2$·6H_2O (168 mg, 0.58 mmol) in H_2O (10 mL) was added to the above solution with stirring. A light-green precipitate of **6** started to form immediately and after ~$^1/_2$ h, the precipitate was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to give a 78% yield. FT-IR (KBr, C═O, cm^{-1}): 1633 (br, s), 1394 (s), 1371 (s). FAB/MS (m/z (%)): 403 $[QA_2Ni+H]^+$ (58). Anal. Calcd (found) for $C_{20}H_{15}N_2O_{5.5}Ni$: C, 55.86 (55.77); H, 3.52 (3.87); N, 6.51 (6.79).

Synthesis of Complex 7·1.5H$_2$O. Quinaldic acid monohydrate (200 mg, 1.15 mmol) was dissolved in H_2O (30 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $MnCl_2$·4H_2O (114 mg, 0.58 mmol) in H_2O (10 mL) was added to the above solution, and a light-orange precipitate started to form immediately. After ~$^1/_2$ h, the precipitate of **7** was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to provide a 79% yield. FT-IR (KBr, C═O, cm^{-1}): 1620 (br, s), 1397 (s), 1380 (s), 1348 (sh). FAB/MS: (m/z (%)): 400 $[QA_2Mn+H]^+$ (32). Anal. Calcd (found) for $C_{20}H_{15}N_2O_{5.5}Mn$: C, 56.35 (56.51); H, 3.55 (3.87); N, 6.57 (6.90).

Synthesis of Complex 8·1.5H$_2$O. Quinaldic acid monohydrate (200 mg, 1.15 mmol) was dissolved in H_2O (30 mL), and a 0.1 N NaOH solution was added to adjust the pH of the solution to 7.0. A solution of $Co(NO_3)_2$·H_2O (169 mg, 0.58 mmol) in H_2O (10 mL) was added to the above solution with stirring. A pink precipitate started to form immediately, and, after ~$^1/_2$ h, the precipitate was filtered, washed with H_2O, CH_3OH, and ether, and dried in vacuo to give a 75% yield. FT-IR (KBr, C═O, cm^{-1}): 1614 (br, s), 1401 (s), 1383 (s), 1351 (s). FAB/MS (m/z (%)): 404 $[QA_2Co+H]^+$ (28). Anal. Calcd (found) for $C_{20}H_{15}N_2O_{5.5}Co$: C, 55.83 (55.96); H, 3.51 (3.93); N, 6.51 (6.74).

X-ray Crystallographic Study of Complex 4·Py. The crystallographic data set for **4·Py** was collected on a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low temperature apparatus using Cu Kα radiation. Only random fluctuations of <1.3% in the intensities of two standard reflections were observed during the course of data collection. The structure was solved by direct methods and refined by full-matrix (based on F) least-squares. An absorption correction (XABS) was applied. Hydrogen atoms were added geometrically, assuming C−H of 0.96 A, and refined using a riding model and isotropic U's equal to 0.025 A^2. In the final cycles of refinement, gallium atoms were refined with anisotropic thermal parameters. A final difference map was essentially featureless. The final coordinates and average temperature factors (U_{eq}) of the atoms in compound **4·Py** are given in the Supporting Information.

Synthesis of PS-Ethyl 2-Quinadate. All the manipulations were carried out under an inert atmosphere. The **PS-CH$_2$Cl** group (4.0 g, 2.5 mmol/g Cl) on macroporous 6% cross-linked polystyrene−divinylbenzene beads, prepared by the Warshawsky method,[14] was swelled in 100 mL of anhydrous DMF for ~$^1/_2$ h, and then a solution of ethyl 2-quinaldate (4.0 g, 20 mmol) in 10 mL DMF was added dropwise. Anhydrous $SnCl_4$ (2 mL) was then added, and the mixture was refluxed under N_2 for ~10 h, after which the beads were filtered, washed well with H_2O and CH_3OH, and dried at 60 °C in vacuo for ~6 h. The FT-IR (KBr) spectrum showed a C═O stretch at 1720 cm^{-1}. Anal. Found: C, 76.93; H, 6.82; N, 0.86; **PS-ethyl-2-QA** 0.6 mmol/g.

Synthesis of PS-Quinaldic Acid. PS-ethyl 2-quinaldate was refluxed with 6 M NaOH for ~5 h. The macroporous beads were then filtered and washed in the following order: H_2O, 0.1 M HOAc, H_2O, and CH_3OH. The beads were finally dried in vacuo at 60 °C for ~6 h. Anal. Found: C, 82.64; H, 7.51; N, 0.86; **PS-2-QA**, 0.6 mmol/g.

Metal Selectivity Study with PS-2-QA. PS-2-QA (50 mg, 0.86 mmol/g N) was added to a 25 mL aqueous solution at pH 3.0 with 10 mM $Al(NO_3)_3$, 10 mM $M(NO_3)_n$ (M = Fe, Cr, Cu, Zn, Mn, and Co), and 1M $NaNO_3$. The mixture was placed on a wrist shaker for ~16 h. The beads were then filtered, washed with H_2O, CH_3OH, and ether, and air-dried. The beads were analyzed for metal concentrations by X-ray fluorescence and atomic absorption spectroscopy (LBNL/Columbia Analytical, Inc).

Recovery Procedure of Al^{3+} Ions. The **PS-2-QA**-Al macroporous polymer beads (50 mg) were added to a solution of H_2SO_4 (1M, 5 mL). The percent recovery of Al^{3+} from the beads was calculated from the residual concentration of Al^{3+} on the beads using inductively coupled plasma analysis (see Figure 3).

Acknowledgment. The reported studies were generously supported by the Office of Environmental Management, Office of Technology Development, Office of Research and Development, Efficient Separations and Processing Program (Teresa B. Fryberger, Program Manager) under U.S. Department of Energy Contract No. DE-ACO3-76SF00098. We thank Andrew Barron, Rice University, for stimulating discussions of this area of research prior to initiating our studies and for the ^{27}Al NMR spectrum of complex **2**.

Supporting Information Available: Table of atomic coordinates and isotropic displacement coefficients for **4·Py** and tables of bond distances, bond angles, and anisotropic displacement coefficients (5 pages). Ordering information is given on any current masthead page.

IC950503J

(14) Warshawsky, A.; Deshe, A.; Gutman, R. *Br. Polym. J.* **1984**, *16*, 234.