**Figure 2.** Stereoview of the unit cell of [Fe(salhis)$_2$]PF$_6$·EtOH, illustrating the hydrogen-bonded layers of cations and solvent. The PF$_6^-$ anions have been omitted for clarity.

The refinement converged at a conventional R value[13e] of 0.072. The final difference-Fourier map showed no peaks greater than 0.53 e/Å$^3$. Final atomic coordinates are given in Table II, while a drawing of the cation illustrating the numbering system is given in Figure 1. Tables of thermal parameters and calculated and observed structure factors are given in the supplementary material.

### Results and Discussion

The crystal structure of [Fe(salhis)$_2$]PF$_6$·EtOH consists of 8 cations, 8 anions, and 8 solvent molecules per unit cell. The PF$_6^-$ anions exhibit some rotational disorder, as evidenced by relatively large anisotropic thermal parameters for the F atoms. Each EtOH of solvation is hydrogen-bonded to three complex cations via two imidazole NH's (N(3) and N(6)) and a phenoxide oxygen (O(1)). This results in layers of [Fe(salhis)$_2$]$^+$ cations, linked by EtOH molecules in the a–c plane (Figure 2) and by PF$_6^-$ anions in the b direction. Each EtOH oxygen atom thus achieves an "ice-like" tetrahedral H-bonded environment.

The [Fe(salhis)$_2$]$^+$ cations exhibit a distorted octahedral FeN$_4$O$_2$ coordination geometry, with the salhis$^-$ ligands arranged in a meridional fashion (Figure 1). This results in the phenoxide oxygens being cis to one another and each being trans to an imidazole group from the same ligand. The two imine nitrogens are therefore trans. Significant distances and angles are given in Table III, while a complete listing of distances and angles and tables of least-squares planes are available in the supplementary material.

The planarity of the salicylaldimine units (C(1)–C(8) and N(1), C(13)–C(20) and N(4); greatest deviation ≤0.1 Å) results in steric constraints that preclude a facial arrangement of the tridentate ligands and accounts for the observed geometry of the complex. The O(1)–Fe–N(2) and O(2)–Fe–N(5) angles are significantly less than 180°, again due to steric constraints of the ligands. The rest of the angles at Fe deviate from those expected for octahedral geometry by ≤4.6°.

Of greatest importance for comparison with EXAFS results on iron proteins are the Fe–O(phenolate) and Fe–N(imidazole) distances, which average 1.914 and 2.147 Å, respectively. These results reinforce the trend of relatively short (≤1.92 Å) phenolate bonds to Fe(III) observed in Fe(saloph)CatH[11] (average 1.905 Å),[14] [Fe(salen)]$_2$hq[11] (average 1.905 Å),[14] and NaFe(*meso*-EHPG)[11] (average 1.907 Å);[15] they also indicate that Fe(III)–N(imidazole) bond lengths (average 2.147 Å) are similar to those observed for Fe–N(pyrazole) bonds (e.g., average 2.165 Å in [Fe(HB(pz)$_3$)(O$_2$CCH$_3$)]$_2$O[16]) and Fe–N(imine) bonds (average 2.123 Å in [Fe(salhis)$_2$]$^+$, average 2.097 Å in Fe(saloph)CatH,[14] and 2.096 Å in [Fe(salen)]$_2$hq[14]). These distances are comparable to those observed by EXAFS for the first-shell scatterers around Fe in the catechol dioxygenases,[10a] transferrin,[10b] and the purple acid phosphatase from beef spleen.[10c] Also of note is the minimal effect of hydrogen bonding to O(1) on the Fe–O bond length,

which is the same for O(1) and O(2) within experimental error.

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### pH-Dependent Metal Ion Selectivity by a Crown Ether Carboxylic Acid

C. Allen Chang,*[†] Jen Twu,[†] and Richard A. Bartsch[‡]

The discovery of neutral cyclic polyethers, crown ethers, was followed by numerous studies in which these compounds were used in the development of ion-selective reagents, biological transport of ions across membranes, phase-transfer catalysis, and a number of other potential analytical and pharmaceutical applications. The intrinsic selectivities of these crown ethers toward metal ions have been attributed to the matching of their cavity sizes and metal ion diameters. Thus, 14-crown-4 is good for Li$^{+1}$ and 18-crown-6 for K$^+$.[2,3] More intensive investigations have revealed that the simple "cavity-size" selectivity concept is not always applicable but is most useful for inflexible homologous systems.

Making structural variations within crown ethers has proven to be a valid technique for producing better ion-selective reagents. The variations include changing the type and the number of donor atoms, adding pendent coordinating groups, and preparing more elaborate macropolycyclic compounds. For example, Gokel et al. prepared several lariat crowns (i.e. crown ethers with neutral binding sites on pendent sidearms) and found that formation constants of their metal complexes are higher than those without sidearms. Presumably this is due to sidearm participation in complexation.[4] It was also found that N-pivot lariat crowns are more flexible and form stronger complexes than C-pivot lariat crowns if the other structures are otherwise similar.[5] On the other hand, if the pendent group has a negative charge, Coulombic interaction between the ligand and metal ion and the resulting charge neutralization provide even stronger complexation; e.g., the formation constant for Na$^+$ complexation by the radical anion form of N-(2-nitrobenzyl)monoaza-15-crown-5 is 25 000 times

(14) Heistand, R. H., II; Roe, A. L.; Que, L., Jr. *Inorg. Chem.* **1982**, *21*, 676–681.

(15) Bailey, N. A.; Cummins, D.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1981**, *50*, 111–120.

(16) Armstrong, W. H.; Spool, A.; Papaefthymion, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653–3667.

†University of Texas at El Paso.
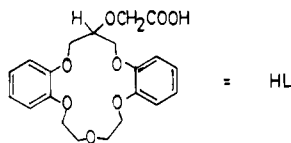‡Texas Tech University.

**Figure 1.** *sym*-Dibenzo-16-crown-5-oxyacetic acid.

greater than that by the neutral form.[6]

Recently, Bartsch et al. reported that the solvent extraction of alkali-metal and alkaline-earth-metal ions using **1** (a crown ether carboxylic acid) and its structural analogue is more efficient than those for analogous compounds without a carboxylic acid pendent group.[7] In competitive extractions of alkali-metal cations, this crown ether carboxylic acid was found to be selective for $Na^+$ at high pH but selective for $K^+$ at pH <6. In this paper, we report a study of the formation constants of complexes of **1** (Figure 1) in both its neutral and its deprotonated forms with $Na^+$, $K^+$, and $Ca^{2+}$. It will be shown that the formation constant is indeed greater for $Na^+$ than for $K^+$ when the ligand is deprotonated.

## Experimental Section

**Materials and Standard Solution.** The ligand *sym*-dibenzo-16-crown-5-oxyacetic acid (**1**) was prepared by the method published previously.[8] It was recrystallized in absolute ethanol and dried under vacuum. NaCl, KCl, and $Ca(NO_3)_2$ salts were obtained as reagent grade compounds. Standard solutions were prepared in dry methanol. Dry methanol was obtained by fractional distillation followed by distillation from magnesium strips under moisture-free conditions.

**Potentiometric Titrations.** A Model 825 MP Fisher pH meter in conjunction with an indicator electrode and a Ag/AgCl reference electrode was employed to monitor the cation activity. For $Na^+$, a sodium ion glass selective indicator electrode was used. A monovalent cation-selective electrode was used for $K^+$. In the case of $Ca^{2+}$, a competitive method against $Na^+$ was designed by using the $Na^+$-selective electrode.[2]

The monovalent electrode has very high selectivity toward $K^+$ ion. For other singly charged cations such as $Li^+$, $Na^+$, $NH_4^+$, and $Rb^+$, selectivity ratios are mainly dependent on the charge density of each ion. In this experiment, $N(CH_3)_4^+$ shows little interference. This is realized not only from its great difference in charge density from the $K^+$ ion but also from the Nernst slopes of the measurements ranging from 54 to 58 mV for a wide range of $K^+/N(CH_3)_4^+$ ratios. The ideal value for the Nernst slope is 59.12 mV for a 10-fold change in activity for practical measurement. The values between 54 and 58 mV are good enough to get reproducible $K$ values, i.e. errors within 3%.

The concentration of each sample was on the order of $10^{-3}-10^{-5}$ M in 1% $H_2O$/methanol solution with no ionic strength adjustment, and the procedure used was similar to a published one[2] using a water-jacketed titration vessel with a 50-mL capacity (Brinkmann).

The equilibria for the complexation reactions between crown ethers and alkali-metal and alkaline-earth-metal ions were very quickly attained.[9,10] The time scale of potentiometric measurements of free alkali-metal ions in methanol solvent has been reported by McClure and Reddy.[11] Their results showed that the electrode attained a potential within 1 mV of the equilibrium values within 5–10 s. In our experiments, electrodes always attained an equilibrium potential within ±0.2 mV within 60–90 s.

The deprotonated form of **1** was generated by adding a stoichiometric amount of $(CH_3)_4NOH$ in methanol. The addition of 1% $H_2O$ to methanol stabilized the titration solvent system to accommodate the situation when deprotonated form of **1** was generated. The $H_2O$/

**Table I.** Formation Constants of Metal Complexes of *sym*-Dibenzo-16-crown-5-oxyacetic Acid[a]

| | ionic diam,[b] Å | log $K_{MHL}^M$ | log $K_{ML}^M$ | Δ log $K$ |
|---|---|---|---|---|
| $Ca^{2+}$ | 2.00 | 2.34 ± 0.12 | 4.10 ± 0.05 | 1.76 |
| $Na^+$ | 2.04 | 2.75 ± 0.03 | 4.02 ± 0.07 | 1.28 |
| $K^+$ | 2.76 | 2.78 ± 0.02 | 3.71 ± 0.02 | 0.93 |

[a] $K_{MHL}^M = [MHL]/[M][HL]$; $K_{ML}^M = [ML]/[M][L]$; 25 °C. [b] Data taken from ref 12. Coordination numbers are assumed to be 6.
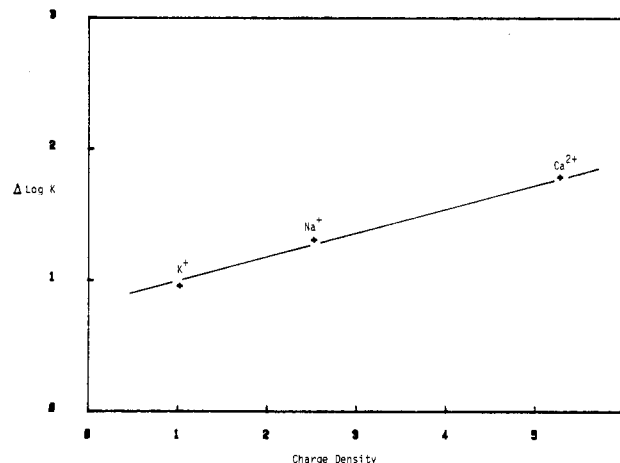
**Figure 2.** Plot of Δ log $K$ vs. charge density (normalized units).

methanol system not only has been adopted by numerous researchers in the field of crown ether complexation chemistry but also solves the solubility problem of **1** in both protonated and deprotonated forms.

The electrodes, buret, and temperature probe were fitted into the titration vessel, and the temperature was maintained at 25 ± 0.1 °C by using a constant-temperature circulating bath. All titrations were performed two or three times, and reproducible results were obtained. The equilibrium calculations were performed with the use of an HP 87 personal computer and computer programs developed in our laboratory. The averaged values are presented together with the standard deviations.

## Results and Discussion

Table I lists the formation constants of **1** with $Na^+$, $K^+$, and $Ca^{2+}$ ions in both the neutral (HL) and deprotonated (L⁻) forms. The logarithmic formation constants (log $K_{MHL}^M$) for all three metal ions with the neutral dibenzo-16-crown-5 ligand **1** are somewhat lower than those of the structural analogue 15-crown-5. (The log $K_{ML}^M$ values for the latter in pure methanol are 3.24, 3.43, and 2.36 for $Na^+$, $K^+$, and $Ca^{2+}$ ions, respectively.[2] The lower formation constants for **1** presumably result from (a) the dibenzo groups of **1**, which make the crown ether more rigid and the crown ether oxygens less basic, (b) the three-carbon bridge in **1**, and (c) values being determined in 1% $H_2O$/methanol, which weakens the ligand–metal binding slightly. Formation constants for complexation of the three metal ions by **1** are in the order $K^+$ ≥ $Na^+$ > $Ca^{2+}$. From examination of Corey–Pauling–Kortun (CPK) space-filling models, the polyether cavity diameter of **1** is estimated to be 1.7–2.0 Å. No correlation between the cavity diameter and the diameter of the metal cations is evident (Table I). However, it does appear that a monovalent cation ($Na^+$) that should fit within the cavity is complexed more strongly by the neutral form of **1** than is a divalent cation ($Ca^{2+}$) of approximately the same size. Similar results have been reported for the complexation of $Na^+$ and $Ca^{2+}$ by 15-crown-5 in methanol[2] and benzo-15-crown-5 in 70% methanol.[13]

When the ligand is deprotonated, the log $K_{ML}^M$ values increase by 8–60-fold. The change is the largest for $Ca^{2+}$ and the least for $K^+$. This enhancement is due to the Coulombic interaction

(1) Olsher, U. *J. Am. Chem. Soc.* **1982**, *104*, 4006.
(2) Gokel, G. W.; Goli, D. M.; Mingani, G.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786.
(3) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; p 145.
(4) Fronczek, F. R.; Gatto, V. J.; Schultz, R. A.; Jungk, W. J.; Colucci, R.; Gandour, R. D.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 6717.
(5) Schultz, R. A.; Dishong, D. M.; Gokel, G. W. *Tetrahedron Lett.* **1981**, *22*, 2623.
(6) Gutowski, D. A.; Echegoyen, L.; Goli, D. M.; Kaifer, A.; Schultz, R. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 1633.
(7) Strzelbicki, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 1894.
(8) Heo, G. S.; Bartsch, R. A.; Schlobohm, L. L.; Lee, J. G. *J. Org. Chem.* **1981**, *46*, 3574.
(9) Chock, P. B. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 1939.
(10) Liesegang, G. W.; Farrow, M. M.; Purdie, N.; Eyring, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 6905.
(11) McClure, J. E.; Reddy, T. B. *Anal. Chem.* **1968**, *40*, 2065.

(12) Shannon, R. D.; *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.
(13) Izatt, R. M.; Terry, R. E.; Nelson, D. B.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7626.

between the charged ligand and the metal ion. Figure 2 shows a plot of $\Delta \log K$ values vs. charge density ($e/d^3$ where $e$ = charge, $d$ = diameter). Indeed, the change in $\log K$ ($\Delta \log K$) in going from the neutral to the deprotonated form is proportional to the charge density; i.e., the larger the charge density, the greater the change. The net result of this effect is the complete reversal of the formation constant ordering, i.e. $Ca^{2+} \geq Na^+ > K^+$. This result is consistent with the competitive extraction data for $Na^+$ and $K^+$ originally reported by Bartsch et al.

In summary, we have demonstrated that by attaching an ionizable pendent group to a crown ether, the ligand selectivity toward metal ion binding can be tuned by simply adjusting the pH of the medium. This mechanism may be very important in biological ion transport through membranes with ionizable ionophores such as monensin and nigericin.

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Contribution from the Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy

# Magnetic Coupling in a Linear-Chain Copper(II)–Imidazolate Compound. Mechanism of the Exchange Interaction through Bridging Imidazolate Ligands

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*Received April 10, 1985*

The crystal structure of *catena*-($\mu$-imidazolato)chlorobis(imidazole)copper(II), CuCl(iz)(izH)$_2$, was reported some years ago,[2] and the compound was found to contain linear chains of imidazolato-bridged copper(II) complexes. In view of the current interest in the characterization of the magnetic properties of one-dimensional magnetic materials[3] and of the mechanism of the exchange interaction between transition-metal ions transmitted by imidazolate and similar bridges,[4-8] we decided to measure the temperature dependence of the magnetic susceptibility of CuCl(iz)(izH)$_2$, and we wish to report here the results of such an analysis, together with an interpretation of the mechanism of exchange on the basis of an extended Hückel treatment.

## Experimental Section

*catena*-($\mu$-Imidazolato)chlorobis(imidazole)copper(II) was prepared according to the reported procedure. The magnetic susceptibility was measured with a Faraday balance, equipped with a Bruker electromagnet, and a R-100 Cahn microbalance. A CF 200 flow cryostat from Oxford Instruments was used to regulate the temperature. EPR spectra were recorded with a Bruker ER 200 spectrometer.

Extended Hückel calculations were performed with a locally generated program. Standard parameters[9] were used for the Cu, N, C, Cl, and H atoms.

## Results and Discussion

The temperature dependence of the magnetic susceptibility of CuCl(iz)(izH)$_2$ in the range 10–300 K is shown in Figure 1. The
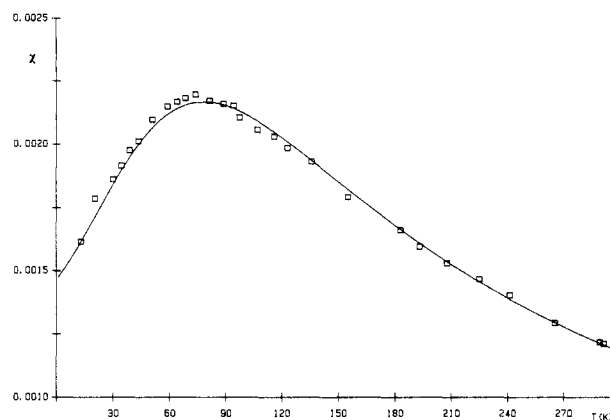
(1) (a) ISSECC, CNR. (b) University of Florence.
(2) Lundberg, B. K. S. *Acta Chem. Scand.* **1972**, *26*, 3902.
(3) "Magneto-Structural Correlations in Exchange Coupled Systems"; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, 1985.
(4) Kolks, G.; Lippard, S. J.; Waszczak, J. V.; Lilienthal, H. R. *J. Am. Chem. Soc.* **1982**, *104*, 717.
(5) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2636.
(6) Benelli, C.; Bunting, R. K.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 3074.
(7) van der Griendt, B.; Hasnoot, J. G.; Reedijk, J.; de Jongh, L. J. *Chem. Phys. Lett.* **1984**, *111*, 161.
(8) Drew, M. G. B.; Nelson, S. M.; Reedijk, J. *Inorg. Chim. Acta* **1982**, *64*, L189.
(9) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.



**Figure 1.** Temperature dependence of the magnetic susceptibility of CuCl(iz)(izH)$_2$ in the 10–300 K range. $\square$ are the experimental points; the curve is calculated with best fit parameters through the Bonner–Fisher model for an $S = {}^1/_2$ antiferromagnetic chain.

**Table I.** Magnetic and Structural Parameters for Imidazolate-Bridged Copper(II) Complexes

| | $J$, cm$^{-1}$ | $\alpha_1{}^a$ | $\theta_1{}^a$ | $\alpha_2{}^a$ | $\theta_2{}^a$ | ref |
|---|---|---|---|---|---|---|
| Cu$_2$bpim$^{3+}$ $^c$ | 163 | 176.2 | 4.7 | 171.1 | 13.4 | 11 |
| Cu$_3$(iz)$_2$(izH)$_8$(ClO$_4$)$_4$ | 117 | 162.9 | 70.0 | 160.9 | 60.0 | 6, 12 |
| CuCl(iz)(izH)$_2$ | 84 | 169.4 | 90.0 | 168.8 | 90.0 | 2, b |
| Cu$_2$(TMDT)$_2$(iz)(ClO$_4$)$_2{}^{+}$ $^d$ | 52 | 161.9 | 91.8 | 160.2 | 90.0 | 4 |
| Cu$_2$(iz)(macro)$^{2+}$ $^e$ | 42 | 158.9 | 68.8 | 166.3 | 79.1 | 13 |
| Cu$_2$(Gly–GlyO)$_2$(iz)$^{-}$ $^f$ | 38 | 157.5 | 5.8 | 157.2 | 10.4 | 14 |

$^a$ The subscripts 1 and 2 refer to the two different metal ions bridged by the imidazolate and are defined in the text. $^b$ This work. $^c$ bpim = 4,5-bis[2-(((2-pyridyl)ethyl)imino)ethyl]imidazolate. $^d$ TMDT = 1,1,7,7-tetramethyldiethylenetriamine. $^e$ macro = the 30-membered "N$_6$O$_4$" macrocyclic Schiff base prepared from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine. $^f$ Gly–GlyO = glycylglycinate.

magnetic susceptibility increases with decreasing temperature down to about 80 K, and below this it decreases, the compound becoming practically diamagnetic below 10 K.

Since the structure indicates a linear chain, the experimental points, in the range 10–300 K, were fit with a Bonner–Fisher treatment,[10] yielding $g = 2.182$ (1) and $J = 84.2$ (1) cm$^{-1}$. Note that we use the Heisenberg spin Hamiltonian in the form: $H = JS_1 \cdot S_2$, a positive $J$ value corresponding to an antiferromagnetic interaction. Below 10 K the magnetic behavior deviates from that expected for a Heisenberg linear chain, indicating that higher order interactions occur. The agreement of the calculated curve with the experimental points can be considered as good, thus confirming the essentially linear magnetic chain behavior of the compound.

The polycrystalline powder EPR spectra of CuCl(iz)(izH)$_2$ recorded at room temperature are fairly broad, with a *quasi* isotropic signal centered at $g = 2.10$. No sharpening is observed on cooling down the sample: the lines remain broad to the point where they disappear due to the antiferromagnetic coupling.

The extent of the coupling is fairly large in CuCl(iz)(izH)$_2$, the second largest thus far reported for copper(II) complexes bridged by imidazolate ligands,[4,6] while a much higher coupling was observed in a case in which the imidazolate moiety is a part of a chelate ligand[4] (see Table I).

The mechanism of the exchange interaction transmitted by a bridging imidazolate has been discussed several times,[4-6] on the basis of qualitative considerations, taking into account the nature

(10) Bonner, J. C.; Fisher, M. E. *Phys. Rev. [Sect.] A* **1964**, *135*, 640.
(11) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079.
(12) Ivarsson, G.; Lundberg, B. K. S.; Ingri, N. *Acta Chem. Scand.* **1972**, *26*, 3005.
(13) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868.
(14) Matsumoto, K.; Ooi, S.; Nakao, Y.; Mori, W.; Nakahara, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2045.