

Crystal structure and electrochemical properties of Cu^{II} complexes with 1,2-bis(2-hydroxybenzamido)benzene

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Abstract—The tetramethylammonium and potassium salts of [1,2-bis(2-oxybenzamido)benzene]copper(II) abbreviated as [NMe₄]₂[Cu(hbab)] and K₂[Cu(hbab)] were prepared and characterized. The x-ray analysis of the potassium salt, K₂[Cu(hbab)] · 5DMF, revealed a unique one-dimensional chain structure consisting of {[KO₃][K(Cu(hbab)O)]_n as the resulting unit, where each K⁺ ion is surrounded octahedrally by six oxygen atoms and all the oxygen atoms play the role of a bridging group to the K⁺ ion. The tetramethylammonium salt, [NMe₄]₂[Cu(hbab)] · H₂O, behaves as a 2:1 electrolyte in the 10⁻³ mol dm⁻³ solutions of methanol, acetonitrile and DMF, while the potassium salt behaves as a 2:1 electrolyte in methanol and as a 1:1 electrolyte in acetonitrile and DMF. The Cu^{II/III} redox potentials of the tetramethylammonium salt in DMF under the presence of 2 equivalent molar of K⁺, Na⁺, and Li⁺ shift to more positive values than those without alkali metal ions, where the magnitude of the positive shift increases with increasing of charge density of alkali metal ion, namely Li⁺ > Na⁺ > K⁺. The charge effect due to ion pair formation between [Cu(hbab)]²⁻ and Na⁺ or K⁺ causes the potential shift, while the potential shift in the case of the Li⁺ ion is brought about by the decrease of donor ability of the phenolic oxygens, besides the charge effect. © 1997 Elsevier Science Ltd

Keywords: crystal structure; electrochemical property; solvent effect; counter cation effect; ion pair formation.

The control of the oxidation state and redox properties of a metal ion by proper ligands attracts much attention, especially in the research field of biomimetic chemistry and functional materials. In this connection, Collins *et al.* designed a series of ligands that can stabilize high oxidation states of metal ions and succeeded in obtaining a variety of metal complexes with high valence state [1,2]. In a series of papers, they reported that the Cu^{II/III} redox potential with N₂O₂ type ligands containing N-amido and oxido donors shifted to a more positive value under the presence of Na⁺ due to the ion pair formation between the complex anion and Na⁺. However, they did not discuss and investigate this phenomenon further.

It is known that the ion pair formation of metal complex with alkali metal ion shows a variety of interesting properties. Floriani *et al.* synthesized the

adducts of cobalt(I)–Schiff base complexes with alkali metal ions and examined the reactivity as exemplified by the reversible formation of the CO₂ complex [3]. The crystal structures of the adducts have been confirmed by the X-ray analyses [3]. Lintvedt *et al.*, studied binuclear copper(II) complexes with 1,3,5-triketones and reported that the one electron reduction potential converted into the sequential two electron reductions and the observed potentials shifted to more positive values when the ion pair between the complexes and Li⁺ or Na⁺ was formed [3,4].

As discussed briefly above, the effect of the ion pair formation on the redox potential is worth investigating for fine-tuning of the redox property and the reactivity of the complex. We chose the copper(II) complex with 1,2-bis(2-hydroxybenzamido)benzene (H₄hbab) and examined the effects of the ion pair formation and solvent on the redox potential, where the ligand system used has strong σ-donor ability to

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stabilize high-oxidation state. We report the synthesis, crystal structure, and effects of the ion pair formation and solvents on redox properties.

EXPERIMENTAL

Materials

All chemicals used for synthetic work were of reagent grade and used without further purification. All solvents used for physical measurements were purified according to literature methods [5] and stored under nitrogen atmosphere.

Preparation of the complexes

1,2-bis(2-hydroxybenzamido)benzene, abbreviated as H₄hbab, was prepared according to the literature [6].

K₂[Cu(hbab)] · 1.5H₂O. Potassium hydroxide (2.20 g, 40 mmol) and H₄hbab (3.48 g, 10 mmol) were dissolved in water (50 ml). Copper(II) hydroxide (1.00 g, 10 mmol) was added to the resulting solution and the mixture was stirred for 1 h with heating (60 ~ 70°C). The insoluble substance was filtered off and the solvent was removed on the rotary evaporator. The residue was crystallized from water and needle-like crystals were obtained. Anal. Calcd for C₂₀H₁₅N₂O_{5.5}K₂Cu: C, 46.81; H, 2.95; N, 5.46. Found: C, 46.67; H, 2.76; N, 5.44. IR/cm⁻¹ ν_{CO} (amide) 1597. μ_{eff} 1.75 BM (300 K).

The DMF solvated compound, K₂[Cu(hbab)] · 5DMF, was obtained from recrystallization of the mixed solution of methanol and DMF and used for the X-ray crystallographic study. Anal. Calcd for C₃₅H₄₇N₇O₉K₂Cu: C, 49.37; H, 5.56; N, 11.51. Found: C, 49.45; H, 5.56; N, 11.36. IR/cm⁻¹ ν_{CO} (amide) 1597. μ_{eff} 1.78 BM (291 K).

[NMe₄]₂[Cu(hbab)] · H₂O. This compound was prepared by the same method as for the potassium salt, using tetramethylammonium hydroxide pentahydrate instead of potassium hydroxide. Recrystallization was made from the methanol solution. Anal. Calcd for C₂₆H₃₈N₄O₅Cu: C, 58.57; H, 6.67; N, 9.76. Found: C, 58.73; H, 6.67; N, 9.62. IR/cm⁻¹ ν_{CO} (amide) 1596. μ_{eff} 1.77 BM (299 K).

Physical measurements

Elemental analyses for C, H and N were carried out at the Elemental Analysis Service Center of Kyushu University. Infrared spectra were recorded on a JASCO A-102 spectrophotometer using KBr discs and electronic spectra were measured on a Hitachi U-400 spectrophotometer using 1 cm quartz cells and *ca* 1 × 10⁻³ mol dm⁻³ solution. Electrical conductivities were measured on a Horiba conductivity meter DS-14 in *ca* 1 × 10⁻³ mol dm⁻³ solution at room temperature.

Electrochemical measurements were carried out on a Yanagimoto P-1100 polarographic analyzer equipped with three electrodes, using a glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference. Tetra-*n*-butylammonium perchlorate (TBAP, *ca* 1 × 10⁻¹ mol dm⁻³) was employed as the supporting electrolyte. Alkali metal cations were added as perchlorate salt. Magnetic susceptibilities were measured on a Faraday balance in the temperature range 80–300 K. The apparatus was calibrated with [Ni(en)₃][S₂O₃] (en = 1,2-diaminoethane) [7]. Diamagnetic corrections were made with Pascal's constants [8]. Effective magnetic moments were calculated using the equation μ_{eff} = 2.828 (χ_AT)^{1/2}, where χ_A is the magnetic susceptibility per copper atom.

X-ray crystallographic study

The relevant crystal data and structural parameters are summarized in Table 1. Single crystals of K₂[Cu(hbab)] · 5DMF were obtained by slow evaporation from the mixed solution of methanol and DMF at room temperature. The crystal with dimensions 0.40 × 0.41 × 0.45 mm was mounted on a glass fiber and coated with epoxy resin. The X-ray diffraction measurements was made on a Rigaku AFC7R four-circle automated diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotating anode generator at 20 ± 1°C using the ω-2θ scan technique. The maximum 2θ value was 55.0° and the scan speed was 16.0°/min (in omega). The unit cell parameters were determined by 25 reflections in the range of 39.5 < 2θ < 40°. The weak reflections

Table 1. Crystal data for K₂[Cu(hbab)] · 5DMF

Formula	H ₄₇ C ₃₅ N ₇ O ₉ K ₂ Cu
Formula weight	851.54
Crystal color	dark purple
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	12.412(3)
<i>b</i> (Å)	12.510(4)
<i>c</i> (Å)	7.383(2)
α (°)	106.69(3)
β (°)	100.44(3)
γ (°)	105.38(2)
<i>V</i> (Å ³)	1016.8(6)
<i>Z</i>	1
d _{cal} (g cm ⁻³)	1.39
d _m (g cm ⁻³)	1.39
Radiation	Mo-Kα
<i>F</i> (000)	445
Number of reflections	4887
Number of unique	4671
Reflections used	<i>I</i> > 3σ(<i>I</i>)
<i>R</i>	0.041
<i>R</i> _w	0.045

($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counting time was 2:1. Of the 4887 reflections, 4671 were unique. The intensities of three representative reflections were measured after every 150 reflections. An empirical absorption correction based on azimuthal scans was applied, where the transmission factors were in the range 0.95–1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by heavy-atom Patterson methods [9] and expanded using Fourier techniques [10]. The thermal parameters of non-hydrogen atoms were refined anisotropically. The thermal parameters of hydrogen atoms were refined isotropically. Full-matrix least-squares refinement was based on 4531 observed reflections ($I > 3.00\sigma(I)$) were employed, where the unweighted and weighted agreement factors of $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$ were used. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin(\theta/\lambda)$ and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber [11]. Anomalous dispersion effects were included in F_{calc} [12]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [13]. The values for the mass attenuation coefficients were those of Creagh and Hubbel [14]. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation [15].

RESULTS AND DISCUSSION

Description of the structure of $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$

Selected bond lengths and angles are listed in Table 2. An ORTEP drawing of $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$ with

Table 2. Selected bond lengths (Å) and angles (°) of $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$

Cu—O1	1.911(4)	K1—O1	2.828(4)
Cu—O2	1.924(4)	K1—O2	2.779(4)
Cu—N1	1.937(4)	K1—O5	2.823(6)
Cu—N2	1.939(4)	K1—O6	2.682(5)
N1—C7	1.330(7)	K1—O8	2.806(5)
N1—C8	1.432(6)	K1—O9	2.701(5)
N2—C13	1.402(6)	K2—O1	2.865(4)
N2—C14	1.357(6)	K2—O2	2.799(4)
K2—O5	2.687(6)	K2—O6	2.873(5)
K2—O7	2.679(6)	K2—O9	2.725(4)
O1—Cu—O2	84.5(2)	Cu—N1—C7	128.2(4)
N1—Cu—N2	86.2(2)	Cu—N1—C8	110.6(3)
O1—Cu—N1	95.1(2)	Cu—N2—C13	110.6(3)
O2—Cu—N2	94.2(2)	Cu—N2—C14	124.8(4)
C7—N1—C8	121.1(4)	C13—N2—C14	120.9(4)

the atom labeling scheme is shown in Fig. 1. Figure 2 shows a one-dimensional chain structure running along the c -axis.

The compound crystallizes in the triclinic space group $P1$. The coordination geometry of copper center is four coordinated square planar, in which four coordination sites are occupied by two deprotonated amido nitrogen atoms and two phenolic oxygen atoms of tetraanionic quadridentate ligand. The bond lengths of Cu—N are within the range of the values found for Cu^{II} complexes with the deprotonated amido nitrogens [16]. The bond lengths of Cu—O are very close to those of [Cu(salen)] [17] and longer than the corresponding values of binuclear Cu^{II}—Cu^{II} complex with the same ligand.

All five DMF molecules per formula unit do not coordinate to Cu^{II} ion. Two of them exist as crystal solvents and the remaining three participate in the formation of the one-dimensional structure by bridging K⁺ ions. Each potassium cation is coordinated by six oxygen atoms consisting of two phenolic oxygens of the quadridentate ligand and four oxygens of four DMF molecules. These K—O distances are in the range of 2.682(5)–2.873(5) Å and the values are close to those of 2.61–2.73 Å found for [Co(pr-salen)KCO₂THF] ($\text{H}_2\text{pr-salen} = \text{N,N}'\text{ethylenebis}(o\text{-hydroxybutylphenonimine})$) [3d] and consistent with the average distance of 2.8 ± 0.1 Å of potassium crown ether complexes [18]. Owing to these K—O bonds, one-dimensional chain structure along the c axis is formed as shown in Fig. 2.

Magnetic properties

The magnetic moments per copper of $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$ are nearly constant from 1.78 BM at 291 K to 1.79 BM at 80 K and close to the spin-only value expected for $S = 1/2$, demonstrating that there exists no magnetic exchange interaction between copper(II) ions through $\{\text{KO}_6\}$ moiety within a chain.

Solvent effect on electrochemical properties

Electrochemical properties and molar electrical conductivity data of the potassium and tetramethylammonium salts in various solvents are given in Table 3. Only the data of $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$ is given, since $K_2[Cu(\text{hbab})] \cdot 1.5\text{H}_2\text{O}$ and $K_2[Cu(\text{hbab})] \cdot 5\text{DMF}$ gave essentially the same results.

Observed potentials are assigned to Cu^{II/III} couple. The Cu^{II/III} couples of all compounds in methanol, acetonitrile and DMF shift to a greater negative potential with increasing dielectric constant or donor strength of the solvent. However, the solvent effect on these potentials is not correlated to the donor number (DN) [19] but to the acceptor number (AN) [19]. A linear correlation between $E_{1/2}$ and AN for $[\text{NMe}_4]_2$

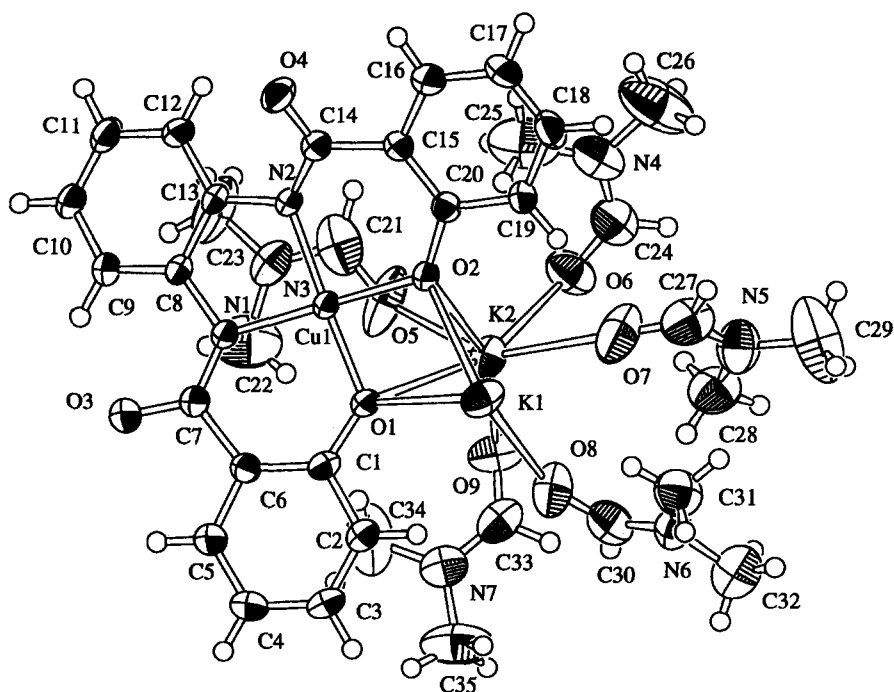


Fig. 1. Molecular structure and atom numbering of $K_2[Cu(hbab)] \cdot 5DMF$.

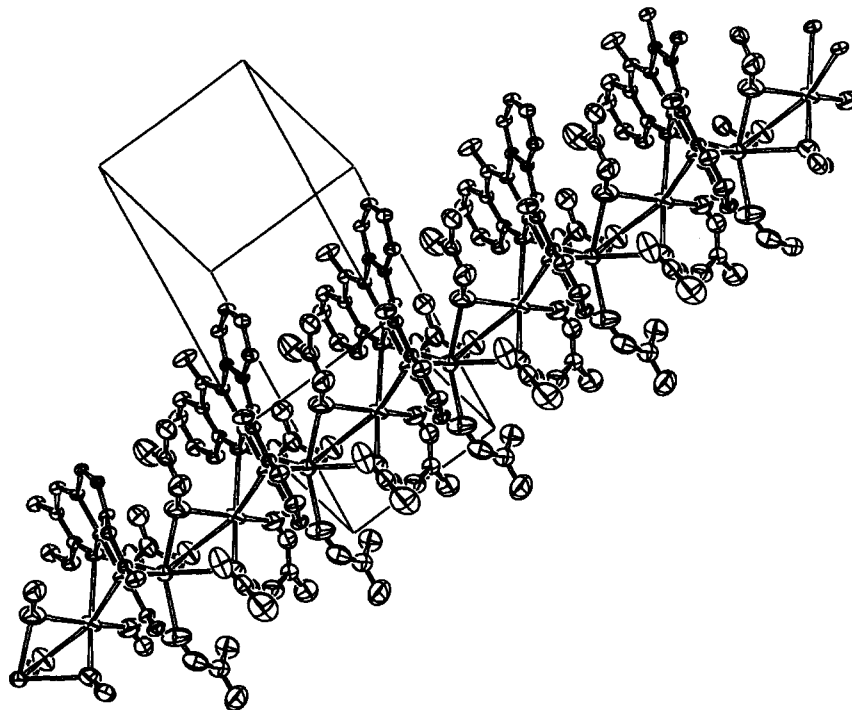


Fig. 2. One-dimensional structure running along the *c*-axis.

$[Cu(hbab)] \cdot H_2O$ is shown in Fig. 3. This is interpreted as follows: the complex anion $[Cu(hbab)]^{2-}$ has two axial sites and solvent molecules might contact the copper center at this site in solution. A $hbab^{4-}$

ligand is a strong donor, owing to deprotonated amide nitrogens and phenolic oxygens, the property as a acceptor of the solvent is more effective on the redox potential than that as a donor.

Table 3. Cu^{II/III} redox potentials^a and molar electrical conductivities of the complexes in methanol, acetonitrile, and DMF

Complex	Solvent	$E_{1/2}$ (V) ^b	E_{pc} (V)	E_{pa} (V)	Λ_M (S cm ² mol ⁻¹)
[NMe ₄] ₂ Cu(hbab)	MeOH	-0.012	-0.041	0.028	162
	AN	-0.275	-0.286	-0.229	332
	DMF	-0.311	-0.341	0.277	125
K ₂ [Cu(hbab)] · 5DMF	MeOH	-0.011	-0.045	0.026	162
	AN	-0.230	-0.266	-0.202	120
	DMF	-0.303	-0.333	-0.267	65.8

^a All potentials were corrected by use of E_{Fc/Fc^+} .

^b $E_{1/2}$ was determined by differential pulse polarography.

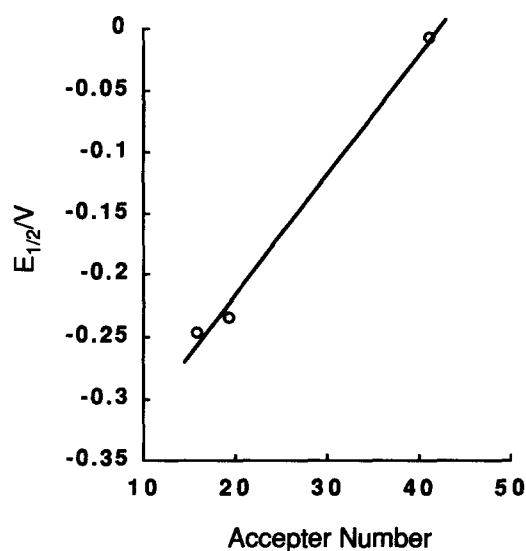


Fig. 3. A correlation between $E_{1/2}$ and AN for [NMe₄]₂[Cu(hbab)] · H₂O, where AN denotes the acceptor number (AN) [19].

Electrolyte behavior of the complexes in several solvents

Electrical conductivity measurements of the potassium and tetramethylammonium salts were carried out in *ca* 10⁻³ mol dm⁻³ solutions of methanol, acetonitrile, and DMF and the results are summarized in Table 3. The data indicates that the potassium salt behaves as a 2:1 electrolyte in methanol and as a 1:1 electrolyte in acetonitrile and DMF, while the tetramethylammonium salt acts as a 2:1 electrolyte regardless of the solvents used [20]. This results indicate that anionic complex [Cu(hbab)]²⁻ with one K⁺ forms an ion pair in acetonitrile and DMF.

As described in the crystal structure of the potassium salt, both two K⁺ ions per formula unit are bound to two phenolic oxygens of [Cu(hbab)]²⁻ anion in the crystal. Therefore, it is reasonable that in acetonitrile and DMF solutions, one of the two K⁺ ions dissociates from [Cu(hbab)]²⁻ and another keeps an

association with the complex to form ion pair species, [Cu(hbab)K(sol)_n]⁻. The electrolyte behavior of the potassium salt does not depend on the dielectric constant of the solvent used, but on whether the solvent is protic or aprotic. The difference of the electrolyte behavior affects the Cu^{II/III} potentials of the complexes. In methanol, $E_{1/2}$ values are nearly constant at *ca* -0.01 V regardless of the counter cation. The $E_{1/2}$ values of the potassium salt in acetonitrile and DMF assume more positive potentials than the corresponding values of the tetramethylammonium salt.

Counter cation effect on redox properties

In order to examine the counter cation effect on the redox properties, the Cu^{II/III} potentials of [NMe₄]₂[Cu(hbab)] · H₂O were measured under the presence of two equiv. of Li⁺, Na⁺, and K⁺ in methanol, acetonitrile, and DMF. The results are given in Table 4. In methanol, $E_{1/2}$ values are nearly constant at *ca* -0.01 V regardless of the presence and type of alkali metal ion. On the other hand, the positive shifts of the potentials were observed in acetonitrile and DMF. Lintvedt and others reported that for Cu^{II/I}, one electron transfer of the binuclear copper(II) complex with 1,3,5-triketones was switched to the sequential two electron transfer and observed potentials were shifted to more positive values under the presence of alkali or alkali earth metal cations [4]. They showed that the magnitude of the shift was highly correlated to the size/charge ratio of the cation. The $\Delta E_{1/2}$ vs ion size in DMF is plotted in Fig. 4, where $\Delta E_{1/2}$ is the potential difference in the presence of the alkali metal ion and that in the absence, and the ionic sizes used are the effective ionic radii for six-coordinated ions reported by Shannon [21]. The linear correlation between $\Delta E_{1/2}$ and ion size is not obtained in this case. The potential in the presence of Li⁺ is 57 mV larger than the value extrapolated from the data for Na⁺ and K⁺. The maximum of *d-d* band for [NMe₄]₂[Cu(hbab)] · H₂O is observed at 553 nm and the maxima under the

Table 4. Cu^{II/III} redox potentials^a of [NMe₄]₂[Cu(hbab)] · H₂O under the presence of alkali metal ions

Cation	MeOH			Acetonitrile			DMF		
	E _{1/2} (V)	E _{pc} (V)	E _{pa} (V)	E _{1/2} (V)	E _{pc} (V)	E _{pa} (V)	E _{1/2} (V)	E _{pc} (V)	E _{pa} (V)
None	-0.012	-0.041	0.028	-0.275	-0.286	-0.229	-0.311	-0.34	-0.277
Li	-0.012	-0.043	0.021	0.011	-0.042	0.038	-0.208	-0.242	-0.168
Na	-0.009	-0.041	0.024	-0.173	-0.201	-0.135	-0.279	-0.310	-0.244
K	-0.007	-0.053	0.022	-0.239	-0.266	-0.201	-0.303	-0.328	-0.261

^a All potentials (V) were corrected by use of E_{Fc^{+/Fc}}.

^b E_{1/2} was determined by differential pulse polarography.

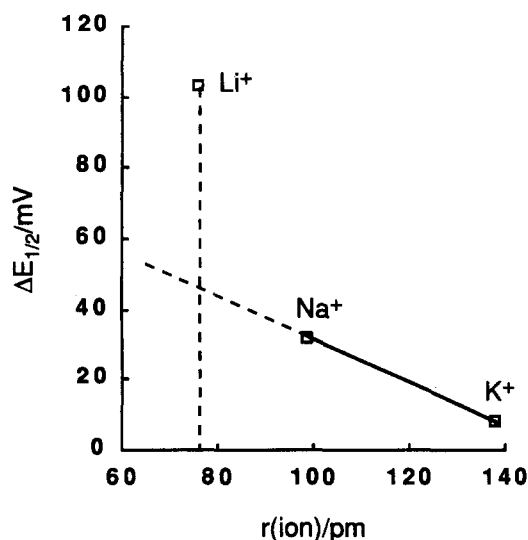


Fig. 4. Plots of $\Delta E_{1/2}$ vs ion size in DMF, where $\Delta E_{1/2}$ is the difference between potentials in the presence and in the absence of alkali metal cations, and the ionic sizes used are effective ionic radii for six-coordinated ions reported by Shannon [21].

presence of Li⁺, Na⁺ and K⁺ are observed at 542, 550 and 551 nm, respectively. The data suggest that in the case of Na⁺ and K⁺, the ion pair formation does not change the coordination geometry and the ligand field strength of [Cu(hbab)]²⁻, so that the charge effect of the alkali metal ion causes the potential shift. Conversely, in the case of Li⁺ ion, the structure of [Cu(hbab)]²⁻ anion gives a change of coordination environment or/and ligand field strength by the formation of [Cu(hbab)Li(sol)_n]⁻ ion pair. It is thought that the potential shift is caused by the donation decrease from phenolic oxygen to copper center due to the electrostatic interaction between phenolic oxygens and Li⁺, in addition to the charge effect.

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