Nonfluorous, Highly CO_2-soluble Chelating Ligands for $scCO_2$ Metal Ion Extraction

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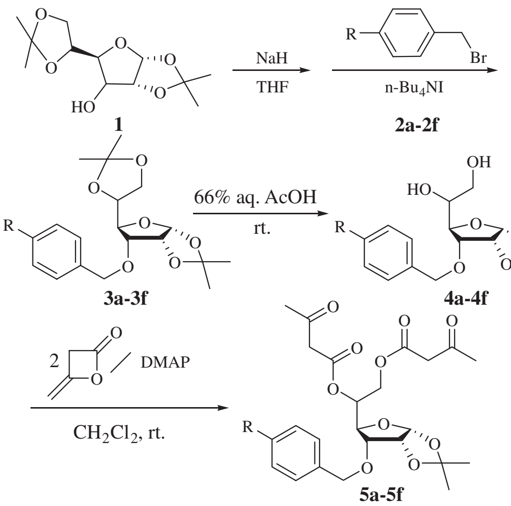
A series of new nonfluorous chelating ligands derived from glucose have been designed and synthesized. All compounds are highly soluble in liquid or supercritical carbon dioxide. Solubility trend of these chelating compounds would be rationalized by the inductive effect of substituent on the benzene ring and the easy accessibility of benzylic ether oxygen and neighboring hydrogens. Preliminary metal ion extraction efficiency test showed that all our compounds are selective for Sr^{2+} and Pb^{2+} extraction.

Supercritical fluids are increasingly used as green media for extraction. By far the most commonly used fluid is CO_2 because it is inexpensive, nontoxic, environmentally benign, and readily available in relatively pure form and has moderate critical constants ($T_c = 304.2\,K$; $P_c = 72.8$ bar, $\rho_c = 0.45\,g\,cm^{-3}$).[1–3] Although supercritical carbon dioxide ($scCO_2$) has been widely used for the supercritical fluid extraction of organic compounds, especially nonpolar compounds, it has difficulty in direct extraction of metal ions because of a charge neutralization requirement and weak solvent–solute interactions.[4,5] To overcome this drawback, many researchers have examined the use of metal-chelating ligands, surfactants, or microemulsions.[6] Some success in extracting metal ions such as K^+, Na^+, Cs^+,[7,8] Cu^{2+},[9,10] Ni^{2+},[11] Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Sr^{2+}, Co^{2+}, Cr^{3+}, Au^{3+}, Bi^{3+}, Fe^{3+}, Sb^{3+}, V^{5+}, Mo^{3+},[12–14] As^{3+},[15,16] Ga^{3+}, and lanthanides,[17,18] has been found using ligands (β-diketones, dithiocarbamates, organic phosphorus acids, crown ether, etc.) via in situ chelation-SFE (supercritical fluid extraction) method. Unfortunately, in most cases, the extraction efficiency is not always good. Therefore, searching new, highly efficient chelating ligands is still a challenge.[19–21]

The mostly used metal-binding ligand is β-diketone reagents because it is readily available and somewhat CO_2-philic.[19] In the present work, we have designed and synthesized a series of new CO_2-philic glucose derivatives containing bis-β-diketone-like functional group, that is bis acetoacetyl group, via simple procedure with high yield. We also report their solubilities and metal ion extraction efficiencies in liquid and supercritical CO_2 (99.99% purity).

The new chelating ligands were synthesized according to the reaction sequences shown in Scheme 1. All the compounds are new except compounds **3c** and **4c** which were prepared by reference method,[22] and their structures were well confirmed by IR, ^1H NMR, ^{13}C NMR, and elementary analysis.



Compounds	5a	5b	5c	5d	5e	5f
R	*t*-Bu	CH_3	H	Br	F	OCF_3

Scheme 1. Synthesis of new chelating ligands.

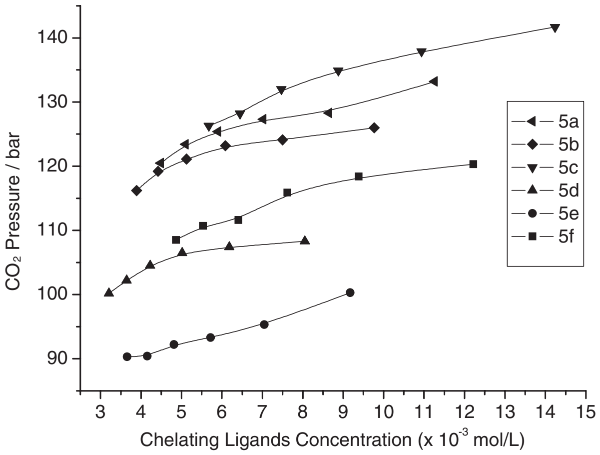


Figure 1. Solubilities of **5a**–**5f** (40 °C).

For observation of dissolution of compounds in $scCO_2$, a high-pressure view cell consisted of a stainless-steel block with two sapphire windows were used. It has an initial volume of 3.61 mL and with a screw tuning the volume to test the cloud point at different volume and pressure. The compounds in the cell were stirred by a magnetic stirring bar. The temperature was controlled using a temperature controller jacket with circulator.

Dissolution conditions of chelating ligands were determined by visual observations using the high-pressure view cell. The solubility results were shown on Figure 1 and the solubility sequence was observed as **5c** < **5a** < **5b** < **5f** < **5d** < **5e**. Even though now we can not rationalize this solubility trend fully, at least we can conclude that the compound with electron-withdrawing substituent on benzene ring has better solubility than the

Table 1. Metal ions extraction efficiency without additive PFOAT[a]

Comp.	[M]:[Comp.]	Metal ion extraction efficiency/%					
		Co	Cu	Sr	Cd	Zn	Pb
5a	1:50	7	9	33	0	0	20
5b	1:50	2	0	4	0	6	9
5c	1:50	2	5	17	18	9	31
5d	1:50	1	3	0	11	0	21
5e	1:50	0	4	0	1	20	17
5f	1:50	0	0	6	0	17	29

[a] 40 °C; CO_2 pressure, 150 bar; stirring for 30 min; 0.01 mL distilled water.

one with electron-donating substituent. It appears that the ether oxygen and benzylic hydrogens next to the ether oxygen enhance the solubility of surfactant through specific Lewis acid–base interactions with CO_2, but only if the ether oxygen and neighboring hydrogens are in a readily accessible position. Especially, the higher solubility of chelating ligands with electron-withdrawing substituent on the benzene ring can be attributed to the higher acidity of benzylic hydrogen and the subsequent stronger interaction with CO_2. Further explanation will be reported in a near future.

All experiments of metal ion extraction from spiked filter paper using the in situ chelation-SFE were performed with a lab-built SFE apparatus described by Wai, et al.[23] Cocktail-like extraction procedure was used for extraction efficiency test. The metal ion extraction efficiency of our chelating ligands was tested with and without PFOAT (tetraethylammonium perfluoro-1-octanesulfonate) as additive. As shown on Table 1, without additive, the extraction efficiencies were very low or negligibly small, indicating that chelating ligands may form complexes with metal ions but either their equilibrium constant might be very small or their solubility in $scCO_2$ is low.[8] In order to increase the extraction efficiency, PFOAT was added as additive. We suggested that the salt dissociates and gives a CO_2-philic $PFOA^-$ anion. The $PFOA^-$ anion undergoes exchange with the Cl^- anion of the complex in the aqueous phase, and consequently the affinity of the complex for $scCO_2$ increases owing to the $scCO_2$-philic $PFOA^-$ chain. As our expectation, the extraction efficiency increased. Interestingly, our new chelating ligands showed selectivity for the extraction of Sr^{2+} and Pb^{2+} (Table 2). A comparing experiment was conducted with PFOAT as the single additive. The result showed that the extraction efficiency was low (at most 30% for Sr^{2+}, Pb^{2+}, and other metal ions) confirming that it is the metal-chelating reagent and not $PFOA^-$ that is doing the extraction.

Table 2. Metal ion extraction efficiency with PFOAT as additive[a]

Comp.	[M]:[Comp.]:[PFOAT]	Metal ion extraction efficiency/%					
		Co	Cu	Sr	Cd	Zn	Pb
5a	1:50:50	3	8	72	8	12	88
5b	1:50:50	36	29	87	38	40	84
5c	1:50:50	2	10	76	32	25	86
5d	1:50:50	21	26	83	0	0	87
5e	1:50:50	10	9	76	0	0	85
5f	1:50:50	1	20	73	5	12	78

[a] 40 °C; CO_2 pressure, 150 bar; stirring for 30 min; 0.01 mL-distilled water.

In summary, we designed and synthesized a series of nonfluorous novel chelating reagents for supercritical carbon dioxide metal extraction. All the newly synthesized ether-containing glucoses with two acetoacetyl groups are highly soluble in liquid or supercritical carbon dioxide. It appears that the ether oxygen and the neighboring benzylic hydrogens will enhance solubility of glucose-derived chelating compounds through Lewis acid–base interaction with CO_2.[3] Solubility trend of our synthetic chelating compounds would be rationalized by the electronic effect of substituent on the benzene ring and the easy accessibility of benzylic ether oxygen and neighboring hydrogens. Our glucose-derived chelating compounds exhibit relative CO_2-philicity; **5c** (H) < **5a** (*t*-Bu) < **5b** (Me) < **5f** (OCF_3) < **5d** (Br) < **5e** (F). Preliminary metal extraction test showed that all our chelating ligands are selective for Sr^{2+} and Pb^{2+} ions. Further studies to explain a detailed relationship between structure and properties (solubility and extraction efficiency) are under going and will be reported.

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