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The inclusion behavior of benzo-15-crown-5 with hydrated transition metal picrates

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Abstract—Six kinds of benzo-15-crown-5 (L) adducts having the stoichiometric formula $M(Pic)_2 \cdot L \cdot xH_2O$ (M=Mn, Cu, x=2; M=Co, Ni, Zn, Cd, x=4; Pic means picrate anion) have been synthesized and characterized by EA, IR, UV and molar conductance. The X-ray crystal structural analysis of the benzo-15-crown-5 adduct with hydrated copper(II) picrate revealed that the benzo-15-crown-5 molecule virtually acts as a second-sphere ligand, which associates with the copper(II) ion by hydrogen bonding of the coordinating water molecule. By the comparison of the IR, UV spectra and molar conductance of the new adducts prepared, it can be deduced that the other adducts exhibit the similar coordination environment to that of the copper adduct. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: copper(II); picrate; crown ether; X-ray; hydrogen bond; crystal structure.

INTRODUCTION

In the process of the chemical extraction of metal ions with crown ether species, picrate is usually used as a hydrophobic counter-anion to carry the host-guest complexes into the organic phase. The extraction mechanism is closely related to the interaction pattern of the picrate complexes of the metal ions with crown ethers. The establishment of the crystal and molecular structures of these complexes indicated that the alkali and alkaline earth metal ions coordinate directly with the crown ether molecules. Nakagawa et al. demonstrated that the solvent extract abilities of aqueous lanthanide picrates with common crown ethers, such as 15-crown-5, 18-crown-6 and their benzo or cyclohexano derivatives, are much lower than those of aqueous alkali- and alkaline-earth-metal picraes, in spite of the apparent matching of the host cavity size and the diameter of the naked lanthanide cation. The low extract abilities are attributed to incomplete dehydration of trivalent lanthanide ions upon extraction [1, 2, 3]. Recently, in the course of our study on the extraction mechanism of hydrated lanthanide picrates with benzo-15-crown-5 (B15C5), a new series of crystalline extracted complexes of hydrated lan-

EXPERIMENTAL

Reagents

All the chemicals used were of reagent grade. B15C5 was recrystallized from *n*-heptane (m.p 79–80°C). Hydrated transition metal (M = Mn, Co, Ni, Cu, Zn and Cd) picrates were prepared by the reaction of picric acid and the corresponding metal carbonates in good yields. Their general formula was determined to be M(Pic)₂ · 6H₂O by elemental analysis.

thanide picrates with B15C5 have been obtained. Xray crystal structural analysis revealed that the B15C5 molecules do not coordinate directly with lanthanide ions, but act as a second-sphere ligand which is associated with lanthanide picrates by hydrogen bonding of coordinating water molecules [4, 5, 6]. These interesting results motivated us to extend our study of the second-sphere coordination of metal crown ether chemistry. In the present paper, we report the synthesis and the characterization of the B15C5 adducts with hydrated transition metal (Mn, Co, Ni, Cu, Zn and Cd) picrates and the crystal structure of the B15C5 adduct with hydrated copper(II) picrate.

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Chemical and physical measurements

Melting points were measured on a WC-1 apparatus and are uncorrected. Transition metal ion contents were determined by EDTA complexometric titration method. Microanalyses (C, H and N) of the adducts were carried out on a Carlo-Erba 1106 elemental analyzer. The IR spectra were recorded on a Shimadzu 435 spectrometer in KBr pellets. UV–VIS spectra were measured with a Shimadzu UV-2100 spectrometer. Conductivity measurements were performed with a DDS-11A conductometer with acetone as solvent at 25°C.

General procedure for the preparation of the adducts

The adducts were prepared by dissolving a 1:2 molar ratio of hydrated metal picrate and B15C5 in a 2:2:1 (v/v/v) mixed solvent of MeCN, EtOH and H₂O, and the resulting solutions were filtered and allowed to stand over several days until the crystalline products of the adducts were separated. A green single crystal of copper(II) adduct suitable for X-ray structural analysis was obtained by recrystallization using the same mixed solvent.

X-ray crystal structure determination of Cu adduct

All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated MoK α radiation and a 12 kW rotating anode generator. Cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 19 carefully centered reflections in the range of 23.23 < 2 θ < 26.73°. The data were corrected for Lorentz and polarization effects and empirical absorption.

The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed on a Micro VAX3100 computer using teXsan crystallographic software package of Molecular Structure Corporation (1985 and 1992). Neutral atom scattering factors were taken from Cromer and Waber. Atomic coordinates and anisotropic temperature factors for all nonhydrogen atoms were refined by full-matrix least-squares.

The crystallographic data and refinement parameters are listed in Table 1. The selected bond distances and angles are given in Table 2

RESULTS AND DISCUSSION

The elemental analysis data as shown in Table 3 indicate that all the adducts prepared have a 1:1 metal picrate–ligand stoichiometry with two or four water molecules, although a mixture of the hydrated tran-

Table 1. The crystallographic data and refinement parameters

Empirical formula	$C_{26}H_{28}N_6O_{21}Cu$
Formula weight	824.08
Crystal color, habit	green, prismatic
Crystal dimensions (mm)	$0.20 \times 0.20 \times 0.30$ mm
Omega scan peak width at	0.32
half-height (°)	
<i>a</i> (Å)	13.542(3)
b (Å)	17.034(7)
<i>c</i> (Å)	7.572(1)
α (°)	90.41(2)
β (°)	100.54(1)
γ (°)	108.31(2)
$V(\text{\AA}^{-3})$	1626.4(8)
Space group	<i>p</i> 1 (#2)
Ζ	2
$D_{\rm calc} ({ m gcm^{-3}})$	1.683
F(000)	846.00
μ (MoK α) (cm ⁻¹)	7.74
$2\theta_{\max}$ (°)	45.0
Total No. of reflections measured	4160
No. observations $[I > 3.00 \sigma (I)]$	3612
R	0.032
R_w	0.049
Maximum peak (e ⁻ Å ⁻³)	0.50
Minimum peak (e ⁻ Å ⁻³)	-0.41

sition metal picrate and ligand in a molar ratio of 1:2 was used.

All the adducts possess similar IR spectra, indicating that they have similar coordination pattern. The IR spectra of the adducts revealed that the molecular symmetric vibration absorption of the ligand at *ca.* 980 cm⁻¹ disappears and that the v_{AR-O-C} absorption at $1250\,\text{cm}^{-1}$ does not undergo any changes in the adducts. The intensity of the $v_{as(C-O-C)}$ absorption at $1120 \,\mathrm{cm}^{-1}$ for the adducts decreases obviously in comparison with that of the free ligand. These results implied that some interaction between hydrated transition metal picrates and aliphatic ether oxygen atoms rather than the phenolic ether oxygen atoms occurs in the adducts. This conclusion will be further confirmed by the X-ray crystal structure analysis of the copper(II) adduct. The strong absorption bands at 3200-3500 cm^{-1} in the adducts show the presence of the water molecules, which is consistent with that of microanalysis.

The measurements of the UV–VIS spectra of the adducts show that all the adducts possess the similar absorption pattern. The absorption for the picrate anion at 320–330 nm does not show much difference before and after the formation of the adducts. This implies that the coordination pattern of the hydrated transition metal picrates does not undergo a pronounced conformational change after the adducts were formed and as a result the central transition

	Bond le	ength (Å)			
Cu–O6	1.941(2)	O4-C11	1.433(4)		
Cu–O7	1.916(2)	O8-H21	0.92		
Cu–O8	1.948(2)	O8-H22	0.95		
Cu–O9	1.937(2)	O9-H23	0.81		
O1–C1	1.425(4)	O9–H24	0.85		
O1–C14	1.411(4)	O4-H21	1.759		
O4–C10	1.426(4)	O1-H22	1.921		
	Bond	angle (°)			
O6–Cu–O7	159.84(8)	O7–Cu–O9	94.04(8)		
O6–Cu–O8	91.13(8)	O8–Cu–O9	160.11(9)		
O6–Cu–O9	87.40(8)	H21-O8-H22	112.7		
O7–Cu–O8	94.13(8)	H23–O9–H24	106.1		

Table 2. Selected bond lengths and angles for the Cu adduct (estimated standard deviations in parentheses)

Table 3. Synthesis, analytical and molar conductivity data of the adducts

Adduct ^a	Yield (%)	M.p. (°C)	Anal. Found (calcd) (%)				Conductivity ^b $(O^{-1} - 1)^{2} = 1$
			С	Н	Ν	М	(<u>12</u> · cm ² mol ·)
$Mn(Pic)_2 \cdot L \cdot 2H_2O$	75	186–188	38.27 (38.29)	3.44 (3.44)	10.38 (10.31)	6.49 (6.74)	35.12 (37.81)
$Co(Pic)_2 \cdot L \cdot 4H_20$	68	164-166	36.45 (36.49)	3.75 (3.74)	9.79 (9.83)	6.49 (6.89)	34.44 (36.48)
$Ni(Pic)_2 \cdot L \cdot 4H_20$	71	142-144	36.53 (36.50)	3.72 (3.74)	9.89 (9.83)	7.01 (6.87)	34.30 (36.62)
$Cu(Pic)_2 \cdot L \cdot 2H_2O$	73	176-178	37.87 (37.86)	3.42 (3.40)	10.18 (10.19)	7.75 (7.72)	15.30 (19.50)
$Zn(Pic)_2 \cdot L \cdot 4H_20$	64	168-170	36.41 (36.22)	3.69 (3.71)	9.83 (9.75)	7.68 (7.59)	20.19 (25.58)
$Cd(Pic)_2 \cdot L \cdot 4H_2O$	65	122–124	34.40 (34.34)	3.51 (3.52)	9.31 (9.25)	12.03 (12.37)	33.43 (36.01)

^aPic is picrate anion, L is benzo-15-crown-5.

^bMeasured in 10^{-3} M acetone solutions at 25°C; the conductivity values of corresponding hydrated transition metal picrates are shown in parentheses.

metal ions may not take part in the direct interaction with the oxygen atoms of crown ether.

The molar conductivity values (as shown in Table 3) for these adducts in acetone are in the range of $15.3-35.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which is the indication of nonelectrolytes for the adducts [7]. Therefore, the transition metal ions in the adducts do not coordinate with the B15C5 molecule directly and no free picrate anion was released, which further supports the results obtained by UV–VIS spectral measurements.

The molecular structure of the Cu adduct is shown in Fig. 1. The adduct consists of two parts, Cu(Pic)₂·2H₂O and B15C5. In the former part, two phenolic oxygen atoms (O6 and O7) in picrate anions and two oxygen atoms (O8 and O9) in water molecules coordinate with central Cu cation, and as result, the coordination number for Cu(II) is 4. The bond lengths for Cu–O6, Cu–O7, Cu–O8 and Cu–O9 are 1.941(2), 1.916(2), 1.948(2) and 1.937(2) Å, respectively. The bond angles of 91.13(8), 94.13(8), 94.04(8) and 87.40(8)° for O6–Cu–O8, O8–Cu–O7, O7–Cu–O9 and O9–Cu–O6, respectively, are near to 90° and the bond angles of 159.84(8) and 160.11(9)° for O6-Cu-O7 and O8-Cu-O9 are less than 180°. Therefore, the coordination about the Cu atom can be considered as a distorted square planar. It is obvious that the latter part, B15C5, does not take part in the coordination with the Cu cation directly. However, it was included in the adduct by hydrogen bonding between one of the coordinating water molecules and two aliphabic ether oxygen atoms (O1 and O4). Two phenolic oxygen atoms in B15C5 do not participate in the formation of hydrogen bond, which is consistent with the result obtained by IR determination. The distance for O1-H22 and O4-H21 are 1.921 and 1.759 A, respectively, which is the indication of the formation of typical hydrogen bonds [8]. Therefore, the water molecule in the adduct virtually acts as a bridge to associate the copper(II) picrate with B15C5 molecule through hydrogen bonding. This kind of inclusion phenomenon of B15C5 is similar to the results of our previous studies on the complexation of hydrated lanthanide picrates with B15C5 [4, 5, 6]. However, it is completely different from the complexation patterns

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Fig. 1. Molecular structure of Cu(Pic)₂ · B15C15 · 2H₂O.

of CuCl₂ and hydrated Cu(ClO₄)₂ \cdot 6H₂O with B15C5, where copper(II) cation was included in the cavity of the B15C5 by direct coordination of crown ether oxygen atoms with Cu(II) ion [9, 10].

On the basis of the crystal structure analysis of the copper adduct and the investigation of IR, UV-VIS spectra and molar conductance of the title adducts, it can be concluded that the coordination ability of the water molecules and picrate anion with transition metal ions are stronger than that of B15C5 molecule, and as a result the hydrated transition metal picrate rather than the transition metal crown ether cationic complex is formed predominately. Due in part to the steric hindrance of the bulky picrate anion and coordinating water molecules around the transition metal ion, the cavity of B15C5 molecule can not accommodate the copper(II) or other transition metal ions directly, although the cavity size of the B15C5 molecule is close to the size of these transition metal ions [9, 10]. Consequently, the B15C5 molecule adopts a special association mode in order to combine with them, i.e. the B15C5 molecule virtually acts as a second-sphere ligand which associates with the hydrated transition metal picrates by hydrogen bonding of coordinating water molecule.

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