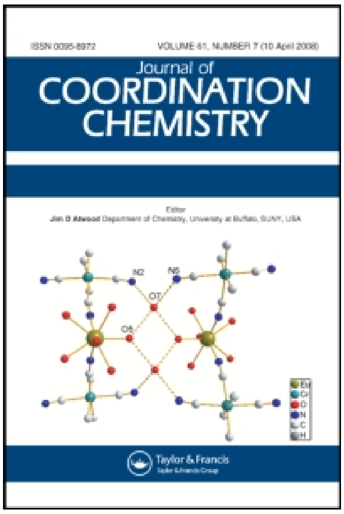

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NOTE

FTIR SPECTROSCOPIC INVESTIGATIONS OF THE COMPLEXATION OF *t*-BUTYLCYCLOHEXANO-15-CROWN-5 WITH DIVALENT TRANSITION METAL IONS

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We have demonstrated the complexation of *t*-butylcyclohexano-15-crown-5 (tBC15C5) to manganese(II) ion when the latter is extracted into carbon tetrachloride with didodecylnaphthalenesulfonic acid (HDDNS) in the presence of tBC15C5.[1] In this system, the weakly coordinating sulfonate anions compete ineffectively with the crown ether for complexation to the manganese(II) centre. Under similar conditions, the ions Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} do not detectably complex to tBC15C5, though extraction results using the same reagents in toluene suggest a weak complex in the case of Zn^{2+} ion.[2] The formation of the manganese(II)–tBC15C5 complex in the HDDNS–tBC15C5 liquid–liquid extraction system is remarkable because it is the first example of a crown ether complexing a divalent first-row transition metal ion under water-saturated conditions. All structurally characterized examples of crown ether complexes of divalent first-row transition metal ions have been prepared under anhydrous conditions.[3–6] Chen *et al.* have presented polarographic and conductometric evidence for the formation of the complexes ML (M = Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}; L = 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6, and dibenzo-24-crown-8) in anhydrous methanol.[7] In this paper, we present FTIR spectroscopic evidence for the complexation of tBC15C5 to the ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}.

EXPERIMENTAL

General Procedures

FTIR spectra were recorded on a Digilab FTS-60 FTIR spectrophotometer, equipped with a modified sample compartment capable of maintaining a constant temperature (25.0 ± 0.5°C). The spectrophotometer was operated in the absorbance mode with a nominal resolution of 2 cm^{-1} using triangular apodization. The sample cell had a pathlength of 1.0 mm and was equipped with barium fluoride windows. All spectra were referenced *versus* the spectrum of the purge gas (dry, CO_2-free air). The spectra of the various solutions in CCl_4 were obtained by subtracting the spectrum of

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pure CCl_4. Baselines were arbitrarily set to zero at 1800 cm^{-1} and 967 cm^{-1} (for water-saturated solutions) or 860 (for dried solutions). Carbon tetrachloride was of spectrophotometric grade (American Burdick and Jackson), while all other chemicals were of reagent grade. 4-*t*-butylcyclohexano-15-crown-5 was obtained from Parish Chemical Co. and was used as received. Didodecylnaphthalenesulfonic acid was obtained from King Industries and was purified by anion exchange chromatography.[8]

Preparation of 0.05 M $M(DDNS)_2$

Fifty cm^3 of a CCl_4 solution of HDDNS (0.1 M) was contacted with 50 cm^3 of 1.0 M $MSO_4(aq)$, (M = Mn, Co, Ni, Cu, or Zn). The two phases were equilibrated by repeated inversion for 30 min at ambient temperature. The aqueous phase was separated from the organic phase, and the latter was treated with fresh 1.0 M MSO_4. This process was repeated until the pH of the aqueous phase reached a (constant) value equal to that of the initial 1.0 M MSO_4 solution. In general, 5 to 10 such equilibrations were required to achieve total loading of the HDDNS solution. In the case of $Mn(DDNS)_2$, the concentration was confirmed by back-extraction of Mn^{2+} ion into 1 M HNO_3, oxidizing with IO_4^-, and spectrophotometrically analyzing the resulting aqueous solution for MnO_4^-;[9] the Mn concentration of the CCl_4 solution (as $Mn(DDNS)_2$) was found to be 0.048 ± 0.003 M. The FTIR spectra of the $M(DDNS)_2$ solutions are devoid of bands in the region 1080–1140 cm^{-1} (Figs. 1a–1j), wherein C–O–C stretching bands for crown ethers are observed.

Reaction of $M(DDNS)_2$ with tBC15C5

Equivalent amounts of $M(DDNS)_2$ and tBC15C5 were mixed together in CCl_4. For water-saturated experiments, the solutions were equilibrated with one drop of aqueous 1 M MSO_4 which had been pre-saturated with tBC15C5 and carbon tetrachloride. The solutions were equilibrated by gently stirring at 25.0 ± 0.2°C for a minimum of 20 h. Samples for FTIR spectroscopic analysis were then withdrawn by pipette. To perform the experiments under conditions of low water activity, the $M(DDNS)_2$–tBC15C5 solutions were transferred to small vials, which were then placed inside a desiccator (equipped with a serum cap) containing P_2O_5 and another small vial containing 1.0 cm^3 of CCl_4. After stirring the sample solutions in the desiccator for a minimum of 20 h,[10] samples were withdrawn by syringe for FTIR spectroscopic analysis. The residual water content in the dried solutions was less than 25 $\mu g\,cm^{-3}$ (0.0014 M) as estimated from the absorbance of the water band at *ca* 3400 cm^{-1} in the FTIR spectra. For a water-saturated $Mn(DDNS)_2$ solution (0.0125 M), the water content was found to be 3960 $\mu g\,cm^{-3}$ (0.22 M), (after correction for the water content of CCl_4) by Karl Fischer titration; this represents 8–9 water molecules per $DDNS^-$ anion.

RESULTS AND DISCUSSION

The macrocyclic polyether tBC15C5 complexes to Mn^{2+} ion under both water-saturated and desiccated conditions. Addition of one equivalent of tBC15C5 to a water-saturated carbon tetrachloride solution of $Mn(DDNS)_2$ results in the formation of a species which displays C–O–C stretching bands at 1088 and 1106 cm^{-1} in the FTIR spectrum (Fig. 1l). No bands are observed for $Mn(DDNS)_2$ (Fig. 1a) in

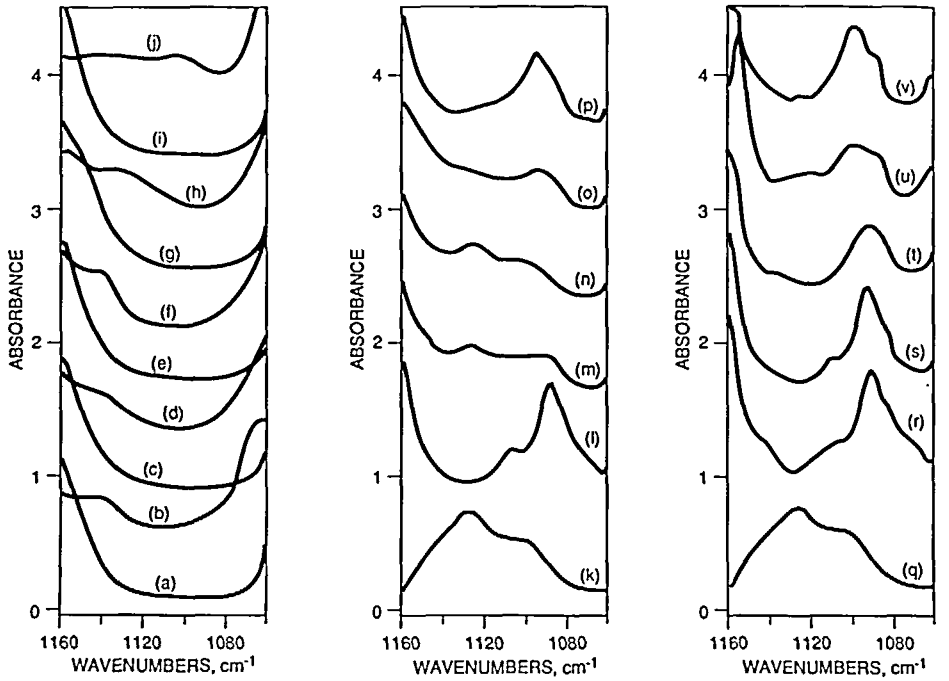

FIGURE 1 FTIR spectra of carbon tetrachloride solutions of (a)–(j): 0.0125 M M(DDNS)$_2$, where M = (a): Mn, water-saturated; (b): Mn, dried; (c): Co, water-saturated; (d): Co, dried; (e): Ni, water-saturated; (f): Ni, dried; (g): Cu, water-saturated; (h): Cu, dried; (i): Zn, water-saturated; (j): Zn, dried; (k): 0.0125 M tBC15C5, water-saturated; (l)–(p): M(DDNS)$_2$ (0.0125 M) plus tBC15C5 (0.0125 M) under water-saturated conditions, where M = (l): Mn; (m): Co; (n): Ni; (o): Cu; (p): Zn; (q): 0.0125 M tBC15C5, dried; (r)–(v): M(DDNS)$_2$ (0.0125 M) plus tBC15C5 (0.0125 M) under dried conditions, where M = (r): Mn; (s): Co; (t): Ni; (u): Cu; (v): Zn. Spectra (b)–(j), (l)–(p), and (r)–(v) have been arbitrarily offset from the baseline for clarity.

this region, and the C–O–C bands of uncomplexed tBC15C5 (Fig. 1k) are absent. Similar observations are made when the solutions are dried over P_2O_5 (vapour-phase equilibration) (Fig. 1b, 1q, 1r). The spectrum obtained upon mixing Mn(DDNS)$_2$ with tBC15C5 under water-saturated conditions closely resembles the spectrum observed earlier upon extraction of Mn^{2+} ion into a mixture of HDDNS and tBC15C5 in CCl_4;[1] in particular, bands at 1088 and 1106 cm^{-1} are observed in both cases. These C–O–C bands are characteristic of a complex in which the Mn^{2+} ion is encircled by the tBC15C5 ligand.[1] Thus, the shifting of the C–O–C stretching bands of the crown ether to the region 1110–1080 cm^{-1} may be taken as an indication of the formation of metal–crown ether complexes of similar structure (*c.f.* Figs. 1k, 1q to Figs. 1l, 1r). Recent X-ray crystallographic studies[11] of the model complex [Mn(C15C5)(H_2O)(DtBNS)][DtBNS] (C15C5 = cyclohexano-15-crown-5; DtBNS = 3,7-Di-*t*-butylnaphthalenesulfonate) indicate a pentagonal bipyramidal coordination geometry about the manganese centre with the equatorial sites being occupied by the five ether oxygen atoms of C15C5. The apical sites are occupied by a water molecule and an *O*-bonded sulfonate anion. For the species observed in solution studies reported here, the exact nature of the ligands bound in apical sites is not known. It is likely that these sites are occupied by water molecules, DDNS$^-$ anions, or both.

In contrast to the case of $Mn(DDNS)_2$, when a CCl_4 solution of $Co(DDNS)_2$ is treated with one equivalent of tBC15C5 under water-saturated conditions, little complexation of the macrocyclic polyether to the cobalt(II) ion is observed. A weak band at 1089 cm^{-1} in the FTIR spectrum (Fig. 1m) suggests some complexation of the crown ether to Co^{2+}, but the bands of free tBC15C5 (Fig. 1k) are not entirely removed. Thus, it can be concluded that the formation constant is smaller than that for the analogous manganese system. This is consistent with what was found in the extraction of Co^{2+} with HDDNS and tBC15C5; *i.e.*, the addition of tBC15C5 to the HDDNS extractant does not result in a synergistic extraction of Co^{2+},[2] and the formation of a cobalt(II)–tBC15C5 complex is not observed by FTIR spectroscopy in the extraction solvent.[1] Yet, upon removal of water cobalt(II)–tBC15C5 complexation is significant as indicated by the appearance of a band at 1092 cm^{-1} (Fig 1s). Thus, tBC15C5 is competing with water for the inner coordination sphere of the cobalt(II) centre.

The $Ni(DDNS)_2$–tBC15C5 system (Fig. 1n, 1t) is similar to the $Co(DDNS)_2$–tBC15C5 system. Under water-saturated conditions, little complexation of tBC15C5 to Ni^{2+} occurs. No bands in the C–O–C stretching region can be identified as resulting from the complexation of Ni^{2+} by tBC15C5 when one equivalent of the crown ether is mixed with $Ni(DDNS)_2$ in CCl_4 under water-saturated conditions (Fig. 1n). However, upon desiccation of the solution, complexation of tBC15C5 to Ni^{2+} is clearly observed (C–O–C stretch at 1092 cm^{-1}) (Fig. 1t).

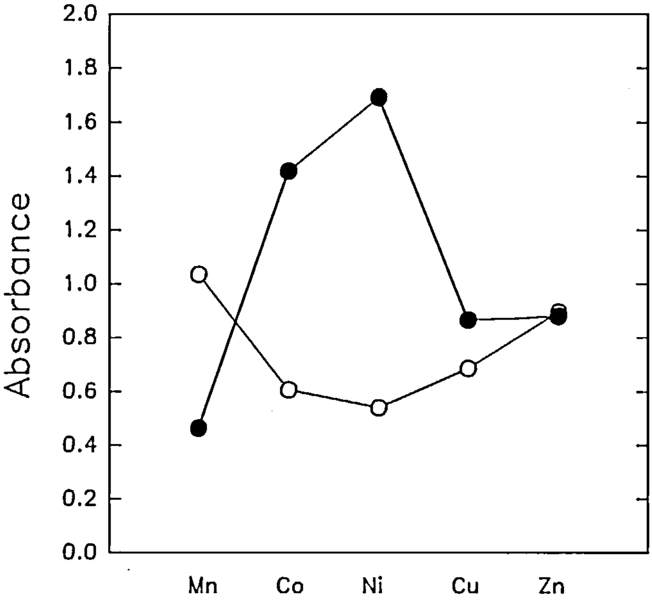

FIGURE 2 Absorbance values for CCl_4 solutions of $M(DDNS)_2$ (0.0125 M) plus tBC15C5 (0.0125 M) at 3500 cm^{-1} and 1088 cm^{-1} for Mn, 1089 cm^{-1} for Co and Ni, and 1094 cm^{-1} for Cu and Zn. The water bands are all broad and are located at 3400 cm^{-1}; since the absorbance values at the peak maxima were high, the values at 3500 cm^{-1} were arbitrarily selected.

The $Cu(DDNS)_2$–tBC15C5 and $Zn(DDNS)_2$–tBC15C5 systems differ somewhat from those discussed above. Namely, the C–O–C stretching bands for the copper–tBC15C5 complex and the zinc–tBC15C5 complex appear at 1094 cm^{-1} with a shoulder at 1088 cm^{-1} in water-saturated solutions (Figs. 1o, 1p) or at 1097 cm^{-1} with a shoulder at 1090 cm^{-1} in dried solutions (Figs. 1u, 1v); the bands are more distinct and intense for zinc *vs* copper. The structural implications of the positions of the C–O–C stretches for these complexes are not clear at present. Attempts are underway in this laboratory to clarify this point by X-ray diffraction analysis of model complexes. Apart from these considerations, Cu^{2+} and Zn^{2+} behave similarly to Co^{2+} and Ni^{2+} in that the complexation seems incomplete under water-saturated conditions but is considerably enhanced on drying.

As shown above, the ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} as sulfonate salts form complexes with tBC15C5 in CCl_4 as determined by FTIR spectrophotometry. Because the extent of complexation increases on drying the solvent, water is an effective competing ligand for these metal ions. This is further illustrated in Fig. 2, which indicates opposing trends in the absorbance for the M^{2+}–tBC15C5 complex (at the C–O–C stretching frequency) and the absorbance for water (O–H stretch measured at 3500 cm^{-1}). In general, a greater degree of complexation of the metal ion by tBC15C5 is accompanied by a decrease in the amount of water present in solution. A qualitative order for the stability of the M^{2+}–tBC15C5 complexes under water-saturated conditions can be deduced from Figs. 1 and 2 as being Mn > Zn > Cu > Co > Ni. That this order follows the reverse of the Irving–Williams order suggests ligand-field considerations are important but in a reverse sense; *i.e.*, ligand-field stabilization energy *decreases* on binding of tBC15C5 to Co^{2+}, Ni^{2+}, or Cu^{2+}. The symmetrical ions Mn^{2+} (d^5) and Zn^{2+} (d^{10}) are not subject to ligand-field stabilization energy effects. Based on the available evidence, this rationalization of the order of complexation appears to be reasonable in view of the pentagonal geometry of the crown ether and weak ligand field of the oxygen donor atoms of the crown ether.[1,2] Currently, experiments are underway to quantitatively measure the stabilities of these complexes.

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