

Reaction of tetrasodiumcalix(4)arene sulphonate with transition metal(III) nitrates (metal = Cr, Co & Fe)

H Mohindra Chawla*, Usha Hooda & Veena Singh

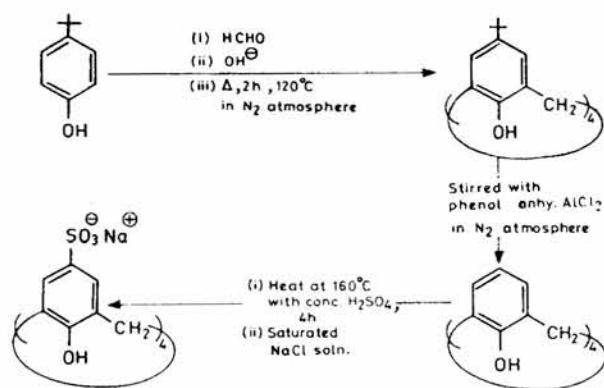
Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

Received 13 October 1993; accepted 12 January 1994

Reaction of tetrasodiumcalix(4)arene sulphonate (TSCS) with metal(III) nitrates (metal = Cr, Co and Fe) provides a good yield of the corresponding complexes, viz., $[\text{Cr}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 10.5\text{H}_2\text{O}$, $[\text{Co}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 7.5\text{H}_2\text{O}$ and $[\text{Fe}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 10\text{H}_2\text{O}$. The new complexes have been characterized by elemental analyses, magnetic susceptibility measurements, IR and electronic spectral data.

The metal aryloxy chemistry has been in vogue since long and extensive reviews on the subject are available¹⁻³. The emphasis in recent years has, however, shifted from simple phenolic analogs to complex natural products and macrocyclic ligands primarily for understanding biological phenomena and ion transport and development of ionophores, siderophores and new materials. The macrocyclic compounds that have been examined in this connection include crown ethers, lariat ethers, cryptates, carcerands⁶ and natural products⁴⁻⁶.

Calix(n)arenes constitute a comparatively new class of phenolic macrocycles that can be obtained from *para* substituted phenols by a series of reactions described in Scheme 1⁷⁻⁹. They possess unique structural features similar to those of cyclodextrins with strong flip flop hydrogen bonding at the lower rim and appendages of hydrophobic functionalities at the upper rim. Usually, calix(n)arenes are high melting and water insoluble compounds but their solubility in water can be increased by replacing the alkyl groups at the upper rim by sulphonate groups. The choice of tetrasodiumcalix(4)arene sulphonate used in the present investigation was based upon our past experience in the field of calix(n)arenes as well as the presence of strongly electron attracting sulphonic acid residues in the upper rim and hydroxyl groups on the lower rim of the calixarene cavity. The presence of both these acidic functionalities in the calix(n)arene molecule offers the possibility of more selective complexation with metal ions as compared to the traditional aryloxy ligands of natural or synthetic origin. Besides these attractive features, the selected ligand is water soluble and can



Scheme 1

be easily synthesized from readily available raw materials.

The selected tetrasodiumcalix(4)arene sulphonate ligand can interact with the metal ion either through the sulphonate bridge or by coordination through oxygen or by forming a host-guest type of complex since it has a cavity in its molecular architecture. It is, therefore, interesting to observe the mode of complexation of the tetrasodiumcalix(4)arene sulphonate with different transition metal ions. In this communication, we describe the reaction of tetrasodiumcalix(4)arene sulphonate with Cr(III), Co(III) and Fe(III) nitrates. The reaction gives good yields of $[\text{Cr}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 10.5\text{H}_2\text{O}$, $[\text{Co}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 7.5\text{H}_2\text{O}$ and $[\text{Fe}(\text{OH}_2)_6][\text{Na}][\text{TSCS}] \cdot 10\text{H}_2\text{O}$ respectively. Further, while determination of X-ray structures of these compounds will require more time (as single crystals of these complexes are difficult to grow), we report their characterization on the basis of ele-

mental analyses, vibrational electronic spectra and magnetic susceptibility data because these complexes can be employed for activation/fixation of functional groups in the substrates.

Materials and Methods

IR spectra of the complexes were recorded in KBr on a Fourier Transform Nicolet-5DX-spectrophotometer in the region 4000-200 cm^{-1} . NMR spectra were recorded on JEOL-99.9 MHz in deuterated chloroform solutions using tetramethylsilane as the internal standard. UV-vis spectra were measured on a Hitachi 330 spectrophotometer. Elemental analyses were carried out by 240 C Perkin Elmer CHN analyser. Melting points were recorded on a digital melting point apparatus (series IA 9100 and IA 9200) and are uncorrected. Magnetic susceptibilities were determined by using a CHAN-2000 magnetic susceptibility balance.

Synthesis of the ligating system

5,11,17,23-Tetra-*p*-tert-butyl-25,26,27,28-tetrahydroxycalix(4)arene was prepared from *p*-tert-butyl phenol and formaldehyde in alkaline medium as reported in the literature⁷, in 50.5% yield; m.p. 346°C (lit. m.p. 344-346°C); UV λ_{max} (CHCl_3) 287 nm and 240 nm; IR (KBr, cm^{-1}) 3150, 1600, 870, 820, 790; MS (*m/z*, % abundance) 648 (100), 647 (35), 592 (17.5), 92 (100), 91 (100).

25,26,27,28-Tetrahydroxycalix(4)arene

A slurry of 5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetrahydroxycalix(4)arene (13.3 g, 20 mmol), phenol (9.02 g, 96 mmol) and anhydrous AlCl_3 (14 g, 10.5 mmol) in toluene (125 ml) was stirred at room temperature for 1 h in nitrogen atmosphere. The mixture was poured into HCl (0.2 N, 250 ml), the organic phase separated and toluene distilled under reduced pressure. Precipitate formed on addition of MeOH, was filtered to obtain 7.54 g of a colourless solid which when crystallized from MeOH- CHCl_3 yielded 6.77 g (78%) of colourless crystals of 25,26,27,28-tetrahydroxycalix(4)arene, m.p. 315-317°C (lit.¹⁰ m.p. 320°C). $R_f = 0.52$ (pet.ether-benzene, 6:4); Analysis: Calc. C, 79.24; H, 5.56. Found: C, 78.97; H, 5.50; IR (KBr, cm^{-1}) 3225, 1600, 1440, 1305, 1050, 920; UV (λ_{max}) 290 nm and 245 nm; PMR (CDCl_3 , δ) 3.95 (s, 8H, ArCH_2Ar), 6.89-7.45 (m, 12H, ArH), 10.02 (s, 1H, D_2O -exchangeable, OH).

Tetrasodiumcalix(4)arene sulphonate (TSCS)

25,26,27,28-Tetrahydroxycalix(4)arene (1.0 g) was treated with conc. H_2SO_4 (10 ml) at 60°C for

4 h. The reaction mixture, after cooling, was added to a saturated NaCl solution (20 ml) when crystals of tetrasodium calix(4)arene sulphonate were formed upon standing (3 days) at room temperature. The separated crystals were filtered and dried (78%). IR (KBr, cm^{-1}) 1220, 1070, 879, 590, 468, 454.

Synthesis of $[\text{Cr}(\text{OH})_6][\text{Na}][\text{calix}(4)\text{arene sulphonate}] \cdot 10.5\text{H}_2\text{O}$

TSCS (0.10 g) dissolved in distilled water (5 ml) was added to a solution of $\text{Cr}(\text{NO}_3)_3$ (0.02 g) in distilled water (5 ml). The pH of the reaction mixture was determined and found to be 7. The solution was slowly evaporated *in vacuo* to get pale blue needles of the compound which were filtered and separated. Analysis: Calc: C, 29.48; H, 4.68. Found: C, 30.25; H, 4.25; m.p., 235-40°C; R_f 0.125 $\text{H}_2\text{O}:\text{MeOH}$; (1:1); IR (KBr, cm^{-1}) 3232, 1660, 1212, 1140, 1080, 950, 880, 872, 850, 593, 578, 458 and 418; UV-vis λ_{max} 25000 cm^{-1} ; magnetic susceptibility 8.118×10^{-6} ($\mu_{\text{eff}} = 4.96$ B.M.).

Synthesis of $[\text{Co}(\text{OH})_6][\text{Na}][\text{TSCS}] \cdot 7.5\text{H}_2\text{O}$

To a solution of TSCS (0.10 g) in distilled water (5 ml) was added a solution of $\text{Co}(\text{NO}_3)_3$ (0.02 g) in distilled water (5 ml). The solution was subjected to slow evaporation, first on a water bath and then in a desiccator, when the cobalt-TSCS complex separated as the pink coloured compound which was filtered and dried, Analysis: Calc: C, 29.55; H, 4.13; Found: C, 30.12; H, 3.92; m.p. 180-82°C; R_f 0.99 in $\text{H}_2\text{O}:\text{MeOH}$ (1:1); IR (KBr, cm^{-1}) 3424, 1660, 1180, 1080, 900, 850, 595, 463 and 416; UV-vis, λ_{max} 25400 cm^{-1} ; magnetic susceptibility 2.818×10^{-6} ($\mu_{\text{eff}} = 2.80$ B.M.).

Synthesis of $[\text{Fe}(\text{OH})_6][\text{Na}][\text{TSCS}] \cdot 10\text{H}_2\text{O}$

To a solution of TSCS (0.10 g) in distilled water (5 ml) was added a solution of $\text{Fe}(\text{NO}_3)_3$ (0.02 g) in distilled water (5 ml). Slow evaporation of the solvent *in vacuo* allowed the isolation of iron-TSCS complex as a colourless solid which was filtered, dried and subjected to analysis. m.p. 245-47°C; R_f 0.037 in $\text{H}_2\text{O}:\text{MeOH}$ (1:1); Calc: C, 28.02; H, 4.33; Found: C, 28.52; H, 4.52; IR (KBr, cm^{-1}) 3456, 1660, 1180, 910, 850, 611, 587, 502, 470, 427, 372 and 356; UV-vis λ_{max} 33333 cm^{-1} ; magnetic susceptibility 136.353×10^{-6} ($\mu_{\text{eff}} = 19.67$ B.M.).

Results and Discussion

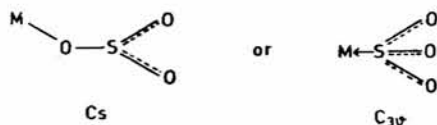
Since TSCS contains both phenolic and sulphonic acid ligating sites, metal ions can complex with either of these groups depending upon the

pH of the reaction. Since the present reactions were carried out in neutral water, appreciable ionization of the phenolic oxygens is not expected under the experimental conditions adopted and, therefore, metal ions may not be covalently linked with the phenolic groups. Such an inference is supported by ion extraction and transport data of alkali metal hydroxides and nitrates from neutral calix(4)arene solutions¹¹. This leaves the possibility of four sulphonate groups at the upper rim of the calixarene molecular basket as the plausible coordination sites. The sulphonate groups can interact with the metal ion through sulphur or through oxygen. It should be possible to differentiate between these two modes of binding by vibrational spectroscopy¹² since it has been observed that coordination through sulphur maintains the symmetry in the free ion while coordination through oxygen lowers the symmetry C_{3v} to C_s to split doubly degenerate vibrations of free ligand into two bands. As a result, coordination through oxygen would shift the S=O stretching band to lower frequencies while coordination through sulphur would shift the S=O stretching vibration to higher frequencies as compared to the position in the free ligand¹². In the present case, $\nu_{S=O}$ band of TSCS appeared at 1070 cm^{-1} which shifted to 1080 cm^{-1} in the case of Cr(III) and Co(III) complexes and 1060 cm^{-1} in case of Fe(III) complex. The lowering of the S=O frequency in the case of iron complex shows that TSCS is holding the $\text{Fe}(\text{OH})_2$ moiety through oxygen of the sulphonate group while in the cases of chromium and cobalt such a coordination is not present.

The elemental analysis of the synthesized complexes, which are air-stable and water-soluble, are in agreement with their suggested compositions. The spectral, magnetic and physical characterization of these complexes are discussed individually.



The pale blue complex, $[\text{Cr}(\text{OH})_2]_6[\text{Na}][\text{TSCS}](\text{acetone}.10.5\text{H}_2\text{O})$; melted at $235\text{--}240^\circ\text{C}$ and showed strong absorptions at 3232 cm^{-1} (anti-symmetric and symmetric OH stretching) and 1660 cm^{-1} (HOH bending) in its IR spectrum revealing thereby the presence of an appreciable amount of coordinated water. The Cr-O absorp-



tions were observed at 458 , 576 and 593 cm^{-1} which compared well with ν_{M-O} data for Cr(III) complexes, obtained with 2,2'-bipyridyl, 1-phenanthroline and some other ligands¹³. Since the $\nu_{S=O}$ and other major absorptions of the ligand were intact in the complex, S-Cr(III) bonding was ruled out. This conclusion was supported by the absence of expected peaks at 1110 , 985 , 633 and 519 cm^{-1} for bonding through S of SO_3Na ¹⁴. The carbonyl frequency of acetone appeared very diffused in the complex and, therefore, revealed that the acetone carbonyl in the complex is either involved in extensive H-bonding or it is embedded in the calixarene cavity as observed earlier by the X-ray structural analysis of molecular complexes of calix(4)arenes with acetone^{10,15}.

The UV-vis spectrum the Cr(III)-TSCS complex showed absorptions at 25000 cm^{-1} which corresponded to a ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition thereby revealing its octahedral geometry¹⁶ which was supported by its magnetic susceptibility value of 8.118×10^{-6} ($\mu_{\text{eff}} = 4.96$ B.M.) and the paramagnetic character of the complex $[\text{Cr}(\text{OH})_2]_6[\text{Na}][\text{TSCS}](\text{acetone}).10.5\text{H}_2\text{O}$.



A similar analysis of the pink coloured Co(III)-TSCS complex revealed that the primary coordination sphere of the Co^{3+} ion is filled by six water molecules. Bands at 3424 and 900 cm^{-1} in the FT-IR spectrum indicated the presence of lattice and coordinated water molecules in the complex. Strong bands at 463 and 595 cm^{-1} confirmed¹³ the coordination of water and metal ion through oxygen. Absence of peaks at 1110 , 985 , 633 and 519 cm^{-1} ruled out the possibility of coordination through¹⁴ S of SO_3Na while its UV-vis spectrum ($\lambda_{\text{max}} 25400\text{ cm}^{-1}$) corresponded to the ${}^4T_{1g} \rightarrow {}^4T_{2g}$ transition for the octahedral geometry which was confirmed by the paramagnetic nature of the complex [magnetic susceptibility value $\approx 2.818 \times 10^{-6}$ ($\mu_{\text{eff}} = 2.80$ B.M.)].



FT-IR analysis of the colourless Fe(III)-TSCS complex revealed that the S=O absorption of the ligand (1070 cm^{-1}) gets shifted to 1060 cm^{-1} in the complex. Strong absorptions at 3456 cm^{-1} confirmed the presence of lattice water while absorption¹² at 587 cm^{-1} confirmed that the coordination of water with the metal ion is through oxygen. The UV-vis spectrum of the Fe(III) exhibited strong absorptions at 3333 cm^{-1} due to the ${}^4T_{1g} \rightarrow {}^6A_{1g}$ transition while its magnetic susceptibility 136.353×10^{-6} ($\mu_{\text{eff}} = 19.67$ B.M.) corre-

sponded to the presence of unpaired electrons in the complex. A comparatively higher value of magnetic susceptibility of this complex showed that the compound may be a possible ferromagnet.

It should be mentioned that the complexity of these compounds prevents normal coordinate treatment and a more quantitative assignments of the frequencies. Since IR assignment for the frequencies is approximate, the assigned structure should be considered as tentative in the absence of an X-ray structure, but these results are required to be published since these complexes promise a good regioselectivity in oxidation reactions of phenolic substrates¹⁷.

Acknowledgement

The authors thank the Department of Science & Technology and Department of Biotechnology, New Delhi for financial assistance.

References

- Mehrotra R C, Gaur D P & Bradley D C, *Metal alkoxides*, (Academic Press, New York), 1978.
- Pierpont C G & Buchanan R M, *Coordination Chem Rev*, 38 (1981) 45.
- Chisholm M H & Rothwell I P, in *Comprehensive coordination chemistry*, edited by J A McCleverty, R D Gillard, & G Wilkinson (Pergamon Press, Oxford) 1987, p 335.
- Flyes T M, *Bioorganic chemistry frontiers*, 1 (1990) 71 and references cited therein.
- Cram D J, *Nature*, 356 (1992) 29.
- Yukito M, Kikuchi J, Ohno T, Hirajama T, Hisaeda Y, Nishimura H, Snyder J P & Steliou K, *J Am chem Soc*, 113 (1991) 8229.
- Gutsche C D, *Calixarenes*, (Royal Society of Chemistry, Cambridge), 1989.
- Gutsche C D & Lin Lee-Gin, *Tetrahedron*, 42 (1986) 1633.
- Gutsche C D, in *Calixarenes a versatile class of macrocyclic compounds*, edited by J Vicens & V Bohmer (Kluwer Academic Publications, Amsterdam), 1991.
- Atwood J L, Orr G W, Means N C, Hamada F, Zhang H, Bott S G & Robinson K D, *Inorg Chem*, 31 (1992) 603.
- Izatt R M, Lamb J D, Hawkins R T, Brown P R, Izatt S R & Cprestension J J, *J Am chem Soc*, 105 (1983) 178 and references cited therein.
- Nakamoto K, *Infrared spectra of inorganic and coordination compounds*, 2nd Edn (John Wiley and Sons, Inc, New York), 1963, p 258.
- Ferraro J R, Driver R, Walker W R & Woznaiak W, *Inorg Chem*, 6 (1967) 1586.
- Newman G & Powell D B, *Spectrochim Acta*, 19 (1963) 213.
- Coleman A W, Bott S G, Morely S D, Means C M, Robinson K D, Zhang J & Atwood J L, *Angew Chem Int Ed Engl*, 27 (1988) 1361.
- Lever A B P, *Inorganic electronic spectroscopy*, (Elsevier, New York), 1968.
- Chawla H M, Hooda U & Singh V, *unpublished results*.