[(η^6-Benzocrown ether)Cr(CO)$_3$] Complexes as FTIR-readable Molecular Sensors for Alkali Metal Cations

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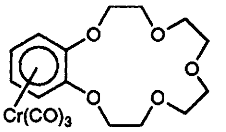
The ν_{CO} modes of [(η^6-benzocrown ether)Cr(CO)$_3$] complexes in methanol and methanol–water solutions shift to higher wavenumber with addition of alkali metal salts to the solution; this wavenumber shift correlates with the cation concentration such that the complexes can be used as molecular sensors for the metal cations.

The ν_{CO} modes of organometalcarbonyl complexes give rise to very strong and sharp absorptions in the IR spectrum, mainly in the 2100–1800 cm^{-1} region,[1,2] a part of the spectrum that is generally free of other absorptions, even in aqueous solution.[3] For these reasons, ν_{CO} modes have been used in the carbonylmetalloimmunoassay (CMIA) technique,[4] in which the intensities of the bands are related to the quantity of trace amounts of organometalcarbonyl-tagged analytes. We have also developed the use of organometalcarbonyl complexes as analytical tools. Our work has concentrated not on the intensities of the ν_{CO} bands, but on shifts in their wavenumbers as a probe of the environment of the metal complex.[5] We have recently shown[6] that carbonylmetal complexes bearing an unsaturated organic ligand with carboxylate or amine substituents can act as pH sensors; upon ionisation of the substituents, either by protonation or deprotonation, the ν_{CO} bands showed wavenumber shifts of up to 20 cm^{-1} which could be correlated with the pH of the solution. In general, this sensing action relies on linking a suitable probe group and an IR-active reporting group (the organometalcarbonyl moiety) *via* a conducting linker, as shown in Fig. 1. Here we report the development of this work for the detection of alkali-metal cations.

In view of the cation-complexing[7] properties of crown ethers, tricarbonylchromium complexes of benzocrown ethers,[8–10] and in particular the complexes[9] [(η^6-benzo-15-crown-5)Cr(CO)$_3$] **1** and [(η^6-benzo-18-crown-6)Cr(CO)$_3$] **2** were identified as suitable {probe group}-{reporting group} assemblies. If a cation such as Na$^+$ is coordinated within the crown, interaction with lone pairs on the two 'catecholic' oxygens would be expected to withdraw electron density from the benzochromium unit, reducing back-donation from the metal to the C–O π^*-antibonding orbitals and raising the wavenumber of the ν_{CO} modes. We have determined the X-ray structure† of **3**, the NaSCN adduct[9] of **1**, and this is shown in Fig. 2 with selected bond lengths. Note in particular that the geometry about O(4) and O(8) is close to trigonal planar indicating sp^2 hybridisation. The p-orbitals on these two oxygens can interact with the arene π-system, thus this geometry is near ideal for the withdrawal of electron density from the tricarbonylchromium moiety by the sodium cation.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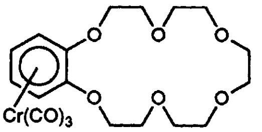
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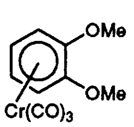
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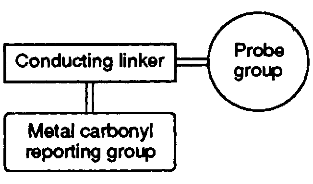

Fig. 1 Schematic representation of a generalised {probe group}-{reporting group} assembly for organometalcarbonyl-based sensors

FTIR spectra of 1.4 mmol dm^{-3} **1** in methanol containing increasing concentrations of Na(ClO$_4$) (0–100 mmol dm^{-3}) are shown in Fig. 3. The two bands correspond to the symmetric and antisymmetric ν_{CO} modes of **1**. The near-isosbestic points indicate the presence of only two significant species in solution: empty **1**, and what we assign as a 1 : 1 **1**-Na$^+$ adduct. The wavenumbers of the band maxima are plotted against sodium concentration in Fig. 4(*a*); the expected shifts to higher wavenumber are observed. Furthermore, the curve indicates that this plot can be used as a titration curve for Na$^+$; hence the wavenumber shifts may be used to determine an unknown sodium ion concentration. The corresponding plot of wavenumber against concentration of KI is shown in Fig. 4(*b*). In this case, the limiting shift of ν^{s}_{CO} is smaller than with sodium, although the crown saturates at lower cation concentrations. This may reflect the likely formation of a 1 : 2 adduct analogous to [(benzo-15-crown-

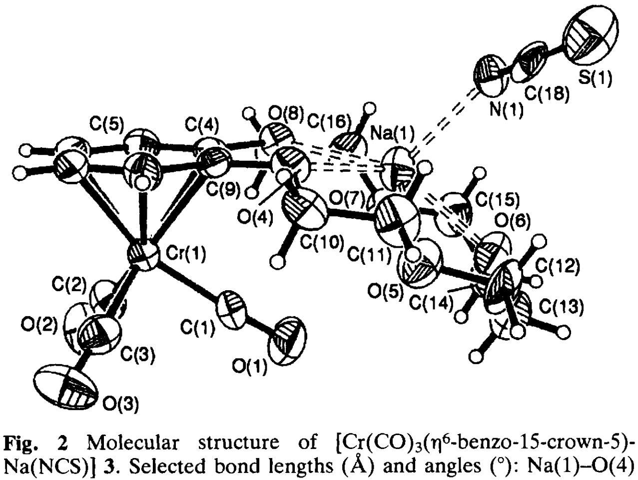

Fig. 2 Molecular structure of [Cr(CO)$_3$(η^6-benzo-15-crown-5)-Na(NCS)] **3**. Selected bond lengths (Å) and angles (°): Na(1)–O(4) 2.442(5), Na(1)–O(5) 2.398(7), Na(1)–O(6) 2.353(6), Na(1)–O(7) 2.417(6), Na(1)–O(8) 2.422(6), Na(1)–N(1) 2.368(10), C(4)–O(8) 1.386(9), C(8)–O(4) 1.373(10), C(9)–O(4)–C(10) 117.2(6), C(9)–O(4)–Na(1) 121.0(4), C(10)–O(4)–Na(1) 114.4(4), C(4)–O(8)–C(17) 116.2(6), C(4)–O(8)–Na(1) 121.3(5), C(17)–O(8)–Na(1) 115.6(4).

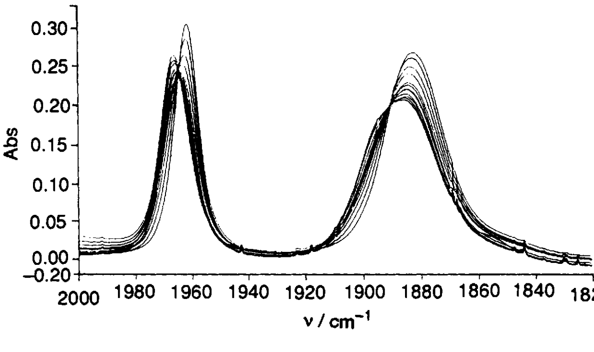

Fig. 3 FTIR spectra of **1** in MeOH containing 0–100 mmol dm^{-3} Na(ClO$_4$)

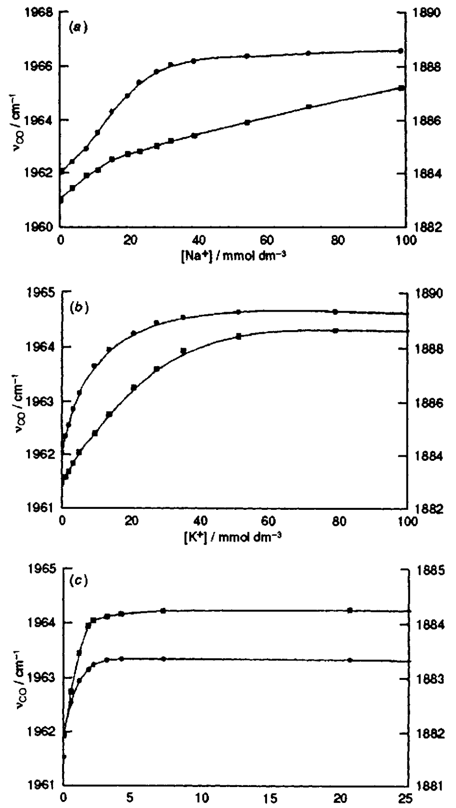

Fig. 4 Plots of ν^s_{CO} ● and ν^{as}_{CO} ■ against metal cation concentration in MeOH: (*a*) 1.4 mmol dm^{-3} **1** with Na(ClO$_4$); (*b*) 1.4 mmol dm^{-3} **1** with KI; (*c*) 0.4 mmol dm^{-3} **2** with Na(ClO$_4$)

5)$_2$K]I, structurally characterised by Mallinson and Truter.[11] A ν_{CO} titration plot for the larger crown complex **2** with Na(ClO$_4$) is shown in Fig. 4(*c*). Crown **2** clearly saturates at much lower sodium concentrations than **1** (*ca.* 6 rather than 40 mmol dm^{-3}); reflecting the known[7] higher stability constant for the (benzo-18-crown-6)Na$^+$ adduct. This result indicates the possibility of optimising the IR readout properties for a given system by the choice of an organometalcarbonyl crown ether derivative with a cation affinity appropriate to the cation concentration range under investigation. Similar experiments using the tricarbonylchromium complex of 1,2-dimethoxybenzene **4**[12] showed only a slight decrease in wavenumber of the ν_{CO} modes as the metal ion concentration increased, confirming that the effects observed with the crown ether complexes were indeed the result of specific crown–cation interactions, rather than simple solvent effects.

Since it is clearly useful to be able to analyse for alkali metal cations in aqueous solution, a further experiment was carried out using solutions of **1** in 50 : 50 methanol–water containing increasing sodium ion concentrations. The plot obtained was similar to that in Fig. 4(*a*), although, as a result of the change in solvent, the crown did not saturate until the sodium ion concentration reached *ca.* 320 mmol dm^{-3}.

These results establish the potential of complexes such as **1** and **2** as a novel type of chemical sensor for alkali metal cations using FTIR detection. In the majority of systems, however, more than one alkali metal will be present, and it would clearly be advantageous to be able to determine simultaneously the concentrations of different cations in the same solution. Preliminary results have shown that the statistical technique of principal component analysis (PCA) applied to FTIR spectra of **1** in methanol solutions containing mixtures of lithium, sodium and potassium can allow the composition of the mixtures to be determined. Further work is being directed towards the development of the PCA method, using two organometalcarbonyl crown ether complexes with differing selectivities for, and vibrational responses to, a range of cations.

We thank the EPSRC (SERC) for financial support.

Received, 13th April 1994; Com. 4/02194K

Footnote

† *Crystal data* for [Cr(CO)$_3$(η^6-benzo-15-crown-5)Na(NCS)]: C$_{18}$H$_{20}$NO$_8$NaSCr, M = 485.40, monoclinic, space group $P2_1/c$, a = 12.654(2), b = 10.709(2), c = 15.976(3) Å, b = 99.47(2)°, U = 2135.43 Å^3, Z = 4, D_c = 1.51 Mg m^{-3}, F(000) = 1000, μ(Mo-Kα) = 0.68 mm^{-1}. Yellow crystal 0.11 × 0.13 × 0.17 mm. 3781 independent reflections measured on Siemens R3m/V diffractometer (Mo-Kα λ = 0.71073 Å, $2 < 2\theta < 50°$, ω-scans). Structure solution by Patterson methods. All non-hydrogen atoms refined anisotropically by full-matrix least-squares analysis; hydrogen atoms were placed in calculated positions. R = 0.0992, R_w = 0.0780, S = 1.19 for 2334 reflections with $|F_o| > 1.8\,\sigma(F_o)$, $w^{-1} = (\sigma^2(|F_o|) + 0.00095|F_o|^2)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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