tially better fit to the experimental data than did those in which inhomogeneous broadening is neglected. The values of the parameters involved in the calculations are listed in Table III and the best fit calculated EPs for S_2^- are shown in Figure 9. Table IV provides a comparison of calculated and experimental overtone intensity distributions of both S_2^- and Se_2^- for selected excitation wavelengths. The following observations may be made:

(1) The quality of the fit of the calculated to the experimental data becomes inferior on the high wavenumber side of the EP maximum. This may be due to contributions to the transition polarizability from higher energy electronic transitions.

(2) The quality of the fit is better for S_2^- than for Se_2^-, which might reflect the greater importance of higher energy contributions for the latter.

(3) The bond length changes attendant upon electronic excitation are similar to that found for iodine[25] (0.35 Å for $^3\Pi_{0u}^+ \leftarrow {}^1\Sigma_g^+$ excitation), but substantially greater than those determined for tetrahedral species (e.g., Δr = 0.09 Å for $[MnO_4]^-$[20] and 0.07 Å for $[MoS_4]^{2-}$[21]). This is due to the much larger reduction in bond order occurring for electronic excitation of diatomic species. Additional evidence for this is furnished by the substantial reduction of the vibrational wavenumber in the excited state, ca. 45% for S_2^- and 40% for Se_2^-. By contrast, the wavenumbers of the totally symmetric fundamentals of tetrahedral molecules decrease by only about 10% on excitation to the lowest energy charge-transfer state.

(25) Herzberg, G. "Spectra of Diatomic Molecules"; Van Nostrand: New York, 1950; p 54.

Conclusion

The results suggest that the ultramarine lattice is an extremely useful matrix with which to trap and to study otherwise unstable inorganic radicals. Its further potential in this respect is the subject of continuing studies.

Acknowledgment. We thank the S.E.R.C. and the University of London for financial support and Reckitt's Colours Ltd. (in particular W. B. Cork) for supplying samples of the various ultramarines and for details on their manufacture.

Registry No. Ultramarine green, 1345-00-2; ultramarine blue, 57455-37-5; ultramarine violet, 12769-96-9; ultramarine pink, 12769-96-9; ultramarine selenium, 86595-02-0.

Notes

Contribution from the Department of Chemistry, University of Otago, Dunedin, New Zealand

Reversed-Phase High-Performance Liquid Chromatography of Cobalt(III) Complexes. Concentration-Dependent Splitting of Single Species

D. A. Buckingham,* C. R. Clark, and R. F. Tasker

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Recently, during studies on ion pair RP-HPLC of Δ-$[Co(en)_2(AA)]^{2+}$ (AA = amino acid) mixtures, we found conditions that allowed single species to completely split into two.[1] This caused us some early misgivings, but the clear advantages this technique has in separating mixtures of closely related cobalt(III) species[2] made us look at this peak-splitting problem in a little more detail. It results from the association of two (or more) complex ions, the ion-pairing reagent and the stationary phase, and is most apparent at low pairing-ion concentrations. It differs from other induced-peak phenomena,[3] which have their origins in sudden solvent–eluent changes; it is potentially more prone to misinterpretation. The following results may be of value to those contemplating the use of RP-HPLC for separating charged metal complexes.

Results and Discussion

Figure 1a shows the rapid and complete separation of five Δ-$[Co(en)_2(AA)]^{2+}$ complexes, in order of elution AA = Gly, Pro, Val, Leu, Phe. When the sample loading is increased at constant ion-pairing conditions (5 mM tosylate, pH 3.50) (Figure 1b,c), the AA = Gly and Pro peaks each split into two with the earlier major components preceding, with progressively shorter retention times (t_R(abnormal)), the minor components, which have normal retention times (t_R(normal)). The degree of splitting, $\Delta t_R = t_R(\text{normal}) - t_R(\text{abnormal})$, is related to the *total amount* of complex loaded rather than to an excess of any one species. Figure 2 demonstrates this with increasing amounts of AA = Pro, causing splitting of the AA = Gly component at constant Gly loading before it itself is split. This effect is clearly distinguished from "normal" overloading, which

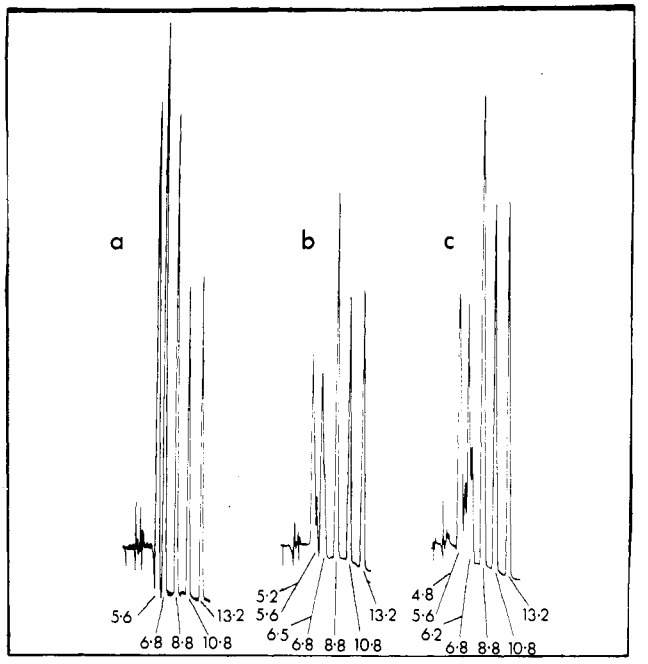

Figure 1. Chromatograms of Δ-$[Co(en)_2(AA)]I_2$ complexes where AA = Gly, Pro, Val, Leu, Phe in order of elution (0–100% $MeOH/H_2O$ eluent over 15 min (linear); 5 mM tosylate, pH 3.5; flow rate 2.5 cm^3 min^{-1}; t_R in min). Increased loadings [(a) 367 nmol (10 μL), (b) 734 nmol (20 μL), (c) 1001 nmol (30 μL)] result in splitting of AA = Gly, t_R(normal) = 5.6, t_R(abnormal) = 5.2 (b), 4.8 (c), and of AA = pro, t_R(normal) = 6.8, t_R(abnormal) = 6.5 (b), 6.2 (c).

(1) Buckingham, D. A.; Clark, C. R.; Tasker, R. F.; Hearn, M. T. W. *J. Liq. Chromatogr.* **1981**, *4*, 689.

(2) The main advantages are speed of separation, resolution, and small sample size (μg–mg).[6] It is to be noted that samples were made up in doubly distilled deionized water and were carefully filtered before injection.

(3) Tseng, P. K.; Rogers, L. B. *J. Chromatogr. Sci.* **1978**, *16*, 436. Stranahan, J. J.; Deming, S. N. *Anal. Chem.* **1982**, *54*, 1540 and references therein.

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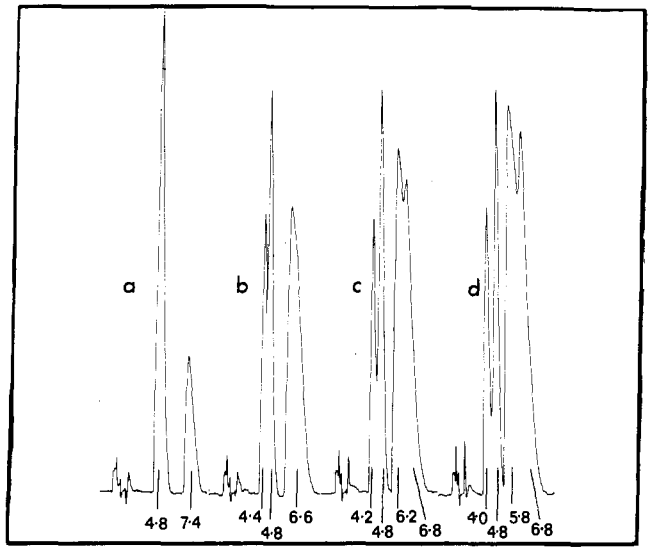

Figure 2. Effect of increased loadings of one species, Δ-$[Co(en)_2(Pro)]I2$, at constant loading of the other, Λ-$[Co(en)_2(Gly)]I_2$ (438 nmol, 30 μL) (3.5% $MeOH/H_2O$ (isocratic); 5 mM tosylate, pH 3.5; flow rate 2.0 cm^3 min^{-1}). Δ-$[Co(en)_2(Pro)]I_2$ loadings (nmol, μL): (a) 270, 5; (b) 1080, 20; (c) 1620, 30; (d) 2160, 40.

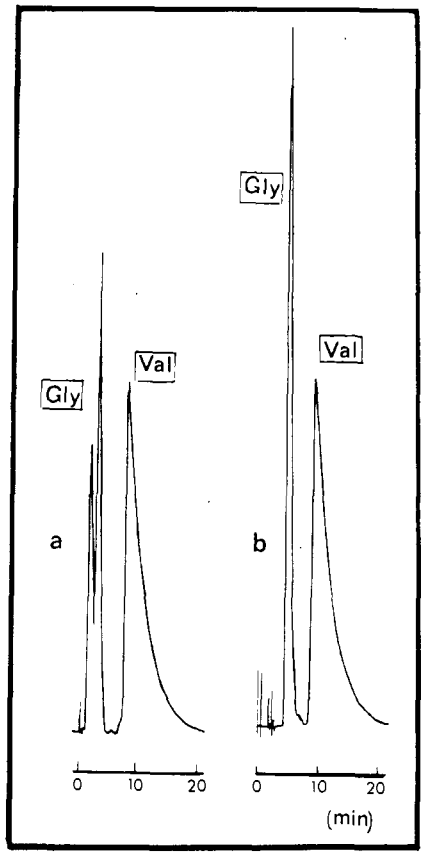

Figure 3. Effect of time delay and overtaking on the stationary phase for Λ-$[Co(en)_2(Gly)]I_2$ (1090 nmol, 10 μL) and Δ-$[Co(en)_2(Val)]I_2$ (3605 nmol, 35 μL) (2.5% $MeOH/H_2O$ (isocratic); 10 mM tosylate, pH 3.5; flow rate 2.0 cm^3 min^{-1}): (a) 10-s delay; (b) 30-s delay.

occurs at even higher loadings and makes its appearance as a broad asymmetric peak preceding, but never completely being separated from, the sharp spike of the normal peak (see Figure 6c). Also, two (or more) different complex cations are required to be present before the "abnormal" effect described here is observed.

It is possible to demonstrate that the splitting is related to events occurring *on the column* and is not related to injection

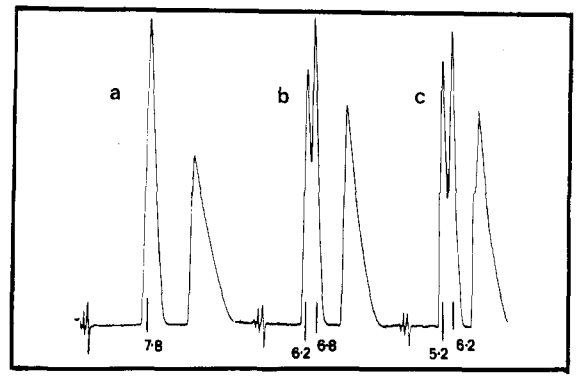

Figure 4. Effect of decreasing pairing-ion concentration for Λ-$[Co(en)_2(Gly)]I_2$ (1640 nmol) and Δ-$[Co(en)_2(Pro)]I_2$ (1616 nmol) (80-μL samples; 2.5% $MeOH/H_2O$ (isocratic); pH 3.5; flow rate 2.0 cm^3 min^{-1}; t_R in min). [Tosylate]: (a) 30 mmol dm^{-3}; (b) 20 mmol dm^{-3}; (c) 15 mmol dm^{-3}.

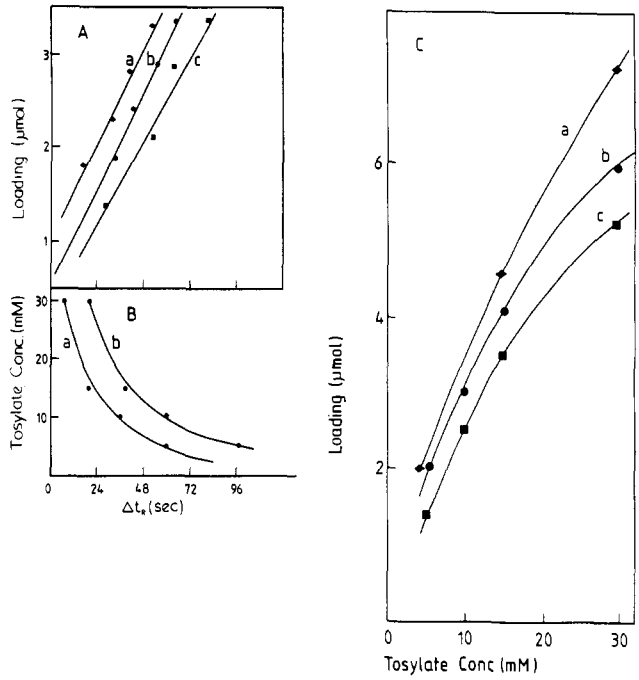

Figure 5. (A) Relationship between Δt_R and loading, where [tosylate] = 10 mM. (B) Relationship between Δt_R and pairing-ion (tosylate) concentration, with (a) = 2000 and (b) = 3000 nmol of Co added. (C) Relationship between loading and [tosylate], with Δt_R = 60 s. Data are for equal amounts of $[Co(en)_2(AA)]^{2+}$ [AA = Gly, Pro (●); AA = Ala, Val (■)] and $[Co(NH_3)_5L]^{2+}$ [L = $CH_3CO_2^-$, $C_2H_5CO_2^-$ (♦)].

problems or to loading abnormalities at the very top of the column. Figure 3 demonstrates this, with part a depicting the chromatogram obtained when AA = Val is loaded first, followed 10 s later by AA = Gly.[4] Obviously the latter overtakes the former on the column and in the process becomes split. If the delay between injections is increased to 30 s, overtaking still takes place but now the AA = Gly peak is not split (Figure 3b). If the amount of AA = Val loaded is increased, then the delay between loadings can be correspondingly increased and Δt_R is maintained. Clearly, the concentration of the solute species in the crossover zone is a factor in determining splitting. If the reverse order of loading is followed, no splitting occurs since the two complex ions never cross.

Splitting is also observed at constant sample loading when the concentration of ion-pairing reagent is lowered. Figure

(4) During this time elution conditions are maintained, and the AA = Val complex will have moved a short distance down the column.

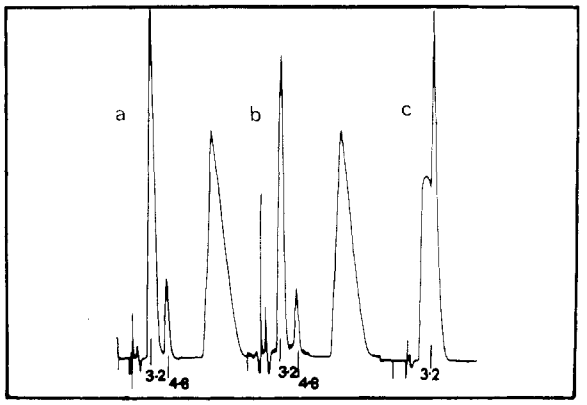

Figure 6. Chromatograms showing the effects of loading ratios and overloading (2.5% MeOH/H_2O (isocratic); 5 mM tosylate, pH 3.5): (a,b) independence of Δt_R (and t_R) of the relative amounts of Λ-$[Co(en)_2(Gly)]I_2$ ((a) 511 nmol, (b) 102 nmol) and Δ-$[Co(en)_2(Val)]I_2$ ((a) 2065 nmol, (b) 2479 nmol) loaded (45-μL samples); (c) "normal" overloading for a single species, Λ-$[Co(en)_2(Gly)]I_2$ (2410 nmol, 40 μL).

4 demonstrates this with decreasing tosylate concentration (from 30 to 15 mM) at a fixed $[Co(en)_2(AA)]^{2+}$ loading (AA = Gly (1640 nmol) + Pro (1616 nmol)). Thus, the effect is also dependent on the concentration of the ion-pairing reagent.

The degree of splitting, Δt_R, increases linearly with amount of sample loaded (n) (Figure 5a) but nonlinearly with ion-pairing concentration ([T]) (Figure 5b), and the combined effect shows as a nonlinear correlation between n and [T] at a fixed Δt_R (Figure 5c). This suggests the onset of saturation of the stationary phase by ion-paired species. From the above data it can be shown that, for a tosylate mobile phase (2.5% MeOH/97.5% H_2O), peak splitting can be avoided (Δt_R < 12 s) if $n/[T] < 1.0 \times 10^{-4}$ dm^3. This is a useful guide for this system, but other results[5] show varying $n/[T]$ minima for other solvent systems and for other ion-pairing reagents.

The phenomenon is not restricted to chiral complexes, as it has been observed for mixtures of the achiral $[Co(NH_3)_5OCOR]^{2+}$ ions (R = CH_3, C_2H_5),[6] but it is independent of the nature of the accompanying anion (I^-, Cl^-, ClO_4^- salts) and of the *ratios* of the complex ions making up the sample. This last point is demonstrated by Figure 6a,b where the Δ-Gly:Δ-Val ratio changes from 0.25 to 0.04 (the total amount loaded remaining constant), but Δt_R remains the same at 96 s. This experiment also allowed the recovery of the separated Λ-Gly peaks, and these were shown to have identical molecular rotations ($[M]_D$ = 1465 ± 15° mol^{-1} dm^3 cm^{-1}) characteristic of pure Λ-$[Co(en)_2(Gly)]^{2+}$;[7] their identity was also confirmed by RP-HPLC of the recovered fractions under conditions where normal behavior obtained. Figure 6c gives the chromatogram of AA = Λ-Gly alone at a much higher loading, and comparisons with peaks a and b show the dramatic difference between the two overloading phenomena.

These experiments show that there must be an interaction between the two (or more) complex ions that influences their distribution ratios with the stationary phase, in addition to the normal pairing-ion depletion effect encountered with high concentrations of sample.[8] Such interactions between the complex cations and pairing anions apparently lead to species of different counterion stoichiometry, or geometry, which have sufficient lifetime on the matrix of the stationary phase to allow their separation as discrete entities.

As mentioned above, this abnormal effect can be avoided by increasing the pairing-ion concentration,[9] but it can also be avoided by using radial-compression columns.[5] In the latter, the distribution of the sample over an annular ring in the loading zone results in an even distribution over a large surface area, whereas for the unsupported stainless-steel columns the sample is highly concentrated in the middle of the zone.

Experimental Section

HPLC was carried out by using a Varian 5000 microprocessor-controlled pump assembly equipped with a Waters Associates C_{18}-μ-Bondapak column (10 μm, 30 cm × 3.9 mm i.d.). Procedures for sample and eluent preparation are detailed elsewhere.[6,10]

(5) Tasker, R. F., unpublished results.
(6) Deva, M.; Clark, C. R.; Tasker, R. F.; Buckingham, D. A. *J. Chromatogr.* **1983**, *262*, 219.
(7) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 4102.
(8) Tomlinson, E.; Jefferies, T. M.; Riley, C. M. *J. Chromatogr.* **1978**, *159*, 315.
(9) We now routinely use 25 mM tosylate for analytical work.
(10) Buckingham, D. A.; Clark, C. R.; Deva, M. M.; Tasker, R. F. *Inorg. Chem.*, companion paper in this issue.

Contribution from the Departments of Chemistry, Montana State University, Bozeman, Montana 59717, and City University of New York, Hunter College, New York, New York 10021

Preparation of Octakis(acetonitrile)dimolybdenum(II) Trifluoromethanesulfonate, Bis(trifluoromethanesulfonato)tetraaquodimolybdenum(II) Trifluoromethanesulfonate, and Molybdenum(III) Trifluoromethanesulfonate

J. M. Mayer† and E. H. Abbott*

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In recent years there has been a great deal of interest in complexes with strong multiple metal–metal bonds,[1] especially the quadruply bonded d^4–d^4 systems.[2] Much of the work has been on the group 6 metals, and a variety of chromium, molybdenum, and tungsten compounds have been made. These seem to fall into a few basic types: complexes with negatively charged bridging ligands (carboxylates), complexes with anionic monodentate ligands (halides and pseudohalides), and mixed compounds with both anionic and neutral donors, of the type $M_2X_4L_4$. One of the more curious aspects is that almost all of the compounds are neutral or negatively charged. If complexes with cationic ligands are excluded, to our knowledge there are only three known cationic dinuclear molybdenum(II) species.

Bowen and Taube have reported Mo_2^{4+}(aq), from which they made $Mo_2(en)_4^{4+}$, precipitated as its chloride salt[3] (en = ethylenediamine). Mo_2^{4+}(aq) has so far defied all attempts at isolation with a noncoordinating anion.[1] $[Mo_2(en)_4]Cl_4$ can also be prepared directly by substitution of $Mo_2Cl_8^{4-}$; this is the only known example of a substitution reaction of a neutral ligand with binuclear molybdenum halides that leaves the quadruple bond intact and does not stop at the neutral species.

Experimental Section

All manipulations were performed by standard Schlenk techniques. Trifluoromethanesulfonic acid (HTFMS) was obtained from the 3M Co. and was distilled prior to use. Trifluoromethanesulfonic anhydride was prepared by distilling the acid from P_2O_5. Formic acid (90%; 10% water) was obtained from Aldrich and was distilled from excess phthalic anhydride; 100% formic acid was stored at 5 °C. Acetonitrile

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