Partial Molar Volumes for Tetracyano(diimine)ferrate(II) Anions in Aqueous Solution

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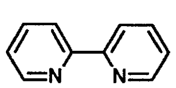
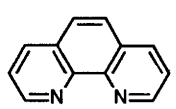
Partial molar volumes have been determined by density measurements for a series of salts $K_2[Fe(CN)_4(diimine)]$. The values for the anions are discussed in relation to analogous tris(diimine)iron(II) cations, and to other inorganic complexes.

Partial molar volumes, V_j, for a wide range of simple inorganic ions in aqueous solution have been available for many years.[1] Such data for inorganic complexes are relatively sparse. Early data related to such complexes as hexa- and octa-cyanometalates;[1,2] data on a number of cobalt(III) and chromium(III) complexes followed.[3] More recently partial molar volumes for several cobalt(III), chromium(III) and palladium(II) complexes have been determined[4] in connection with the establishment of activation volumes and volume profiles for substitution at these centres. We have determined partial molar volumes for some iron(II)–diimine complex cations of the $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) type, in water and in aqueous methanol.[5] These partial molar volumes did not correlate with intrinsic ligand and complex volumes, so we wished to extend our investigation in an attempt to unravel intrinsic and solvation effects. In practice there are certain practical difficulties associated with the required precise determination of densities for solutions of salts of iron(II)–diimine cations, and we therefore turned our attention to the series of $[Fe(CN)_4(L\text{–}L)]^{2-}$ anions with L–L = one of the diimine ligands L^1–L^5 or ethane-1,2-diamine (L^6). The potassium salts of these anions can be prepared in a pure state and are sufficiently soluble in water for accurate density measurements. This series presents the additional advantage of including the particularly small $[Fe(CN)_4(HN{=}CHCH{=}NH)]^{2-}$ anion; the tris(ligand) analogue $[Fe(HN{=}CHCH{=}NH)_3]^{2+}$ has yet to be prepared.[6]

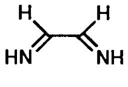
In this paper we report the results of our establishment of partial molar volumes for these ternary anions, discussing our results in relation to values for the $[Fe(diimine)_3]^{2+}$ series and other inorganic complexes, and to intrinsic ligand and complex properties such as relative molecular masses and volumes.



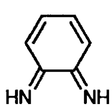
L^1 (bipy)



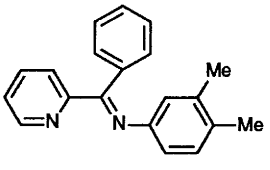
L^2 (phen)



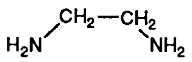
L^3



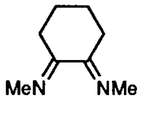
L^4



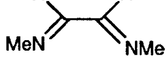
L^5



L^6 (en)



L^7



L^8

Experimental

The complexes were prepared by suitable modifications of Schilt's method, *via* the respective tris(ligand) complexes.[7] These tris(Schiff base) iron(II) complexes were prepared by established methods.[8] Products were characterised by iron (atomic absorption spectrometry) and C, H and N analyses and from their UV/VIS spectra as appropriate. These ternary complexes are strongly solvatochromic,[9] so they can be well characterised in terms of their ν and ε values in several solvent media. The numbers of water molecules of crystallisation were determined from the C, H and N analyses, by thermogravimetry, or through X-ray crystal structure determination.[10]

Densities were measured, and partial molar volumes for the respective salts derived, using the apparatus and calculations described earlier.[5] All measurements were made at 298.15 K.

Results

The compounds studied and the range of concentrations over which solution densities were measured are given in Table 1. The two most soluble salts, those containing the ligands L^6 and L^3, gave tolerably good plots of densities (apparent molar volumes) against salt concentration (see the example in Fig. 1), and it was therefore possible to estimate partial molar volumes using the Redlich–Meyer equation[11] to extrapolate to zero ionic strength. This is shown for $K_2[Fe(CN)_4(L^3)]\cdot 4H_2O$ in Fig. 1. For the other compounds, where density *vs.* concentration plots were slightly more scattered, a mean density was used to calculate the partial molar volume of each salt hydrate. The variation of density with concentration is, of course, very small, so the difference between these methods corresponds to

Table 1 Partial molar volumes, V_j, for ternary iron(II)–diimine–cyanide complexes, in aqueous solution at 298.2 K

			V_j/cm^3 mol^{-1}	
Compound	M_r of anion	Concentration range[a] (no. of experiments)	Potassium salt[b]	Anion[c]
$K_2[Fe(CN)_4L^3]\cdot 4H_2O$	216	3.6–13.1 (7)	105 ± 3 ($c \longrightarrow 0$)	87
$K_2[Fe(CN)_4L^6]\cdot 4H_2O$	220	6.0–15.4 (5)	119 ± 3 ($c \longrightarrow 0$)	101
$K_2[Fe(CN)_4L^4]\cdot 3H_2O$	266	3.7–10.8 (8)	116 ± 6 (mean)	98
$K_2[Fe(CN)_4L^1]\cdot 3H_2O$	316	3.1–9.2 (12)	199 ± 8 (mean)	181
$K_2[Fe(CN)_4L^2]\cdot 4H_2O$	340	5.9–9.1 (5)	198 ± 4 (mean)	180
$K_2[Fe(CN)_4L^5]\cdot 2H_2O$	446	2.9–10.8 (7)	257 ± 4 (mean)	239

[a] 10^3 (salt concentration/mol kg^{-1}). [b] $c \longrightarrow 0$ indicates extrapolation to infinite dilution. These values apply to the respective anhydrous salts (see text). [c] Assuming $V_j(H^+) = 0$ (see text).

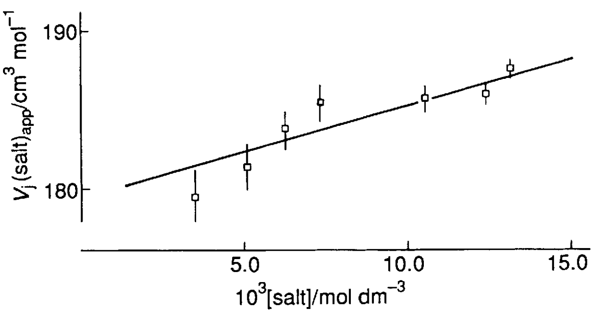


Fig. 1 Plot of apparent partial molar volume against concentration for the salt $K_2[Fe(CN)_4L^3]\cdot 4H_2O$. The error bars are estimates, reflecting the greater difficulties of determining density differences between salt solution and water at low concentrations of salt

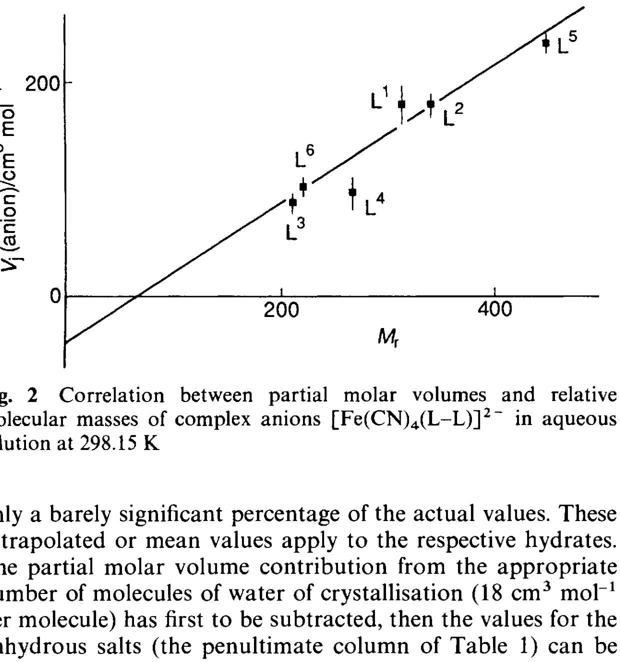


Fig. 2 Correlation between partial molar volumes and relative molecular masses of complex anions $[Fe(CN)_4(L\text{–}L)]^{2-}$ in aqueous solution at 298.15 K

only a barely significant percentage of the actual values. These extrapolated or mean values apply to the respective hydrates. The partial molar volume contribution from the appropriate number of molecules of water of crystallisation (18 cm^3 mol^{-1} per molecule) has first to be subtracted, then the values for the anhydrous salts (the penultimate column of Table 1) can be separated into cation and anion (the final column of Table 1) contributions.[12]

Discussion

Before discussing our results, it is necessary to consider the question of assignment of single-ion values. The usual convention is to take the partial molar volume of hydrogen ion, $V_j(H^+)$, as zero, as in Millero's classic and extensive review.[1] If we are to compare anion and cation volumes, as in discussing the two series of iron(II) complexes under consideration, then an estimate for the absolute value of $V_j(H^+)$ is needed. The majority of authors favour a value close to -5 cm^3 mol^{-1}, but values up to about $+5$ cm^3 mol^{-1} have been proposed.[13] If, however, one uses the TATB assumption, so popular for single-ion thermodynamic transfer parameters,[14] then $V_j(AsPh_4^+) = V_j(BPh_4^-)$ leads to $V_j(H^+) = -11$ cm^3 mol^{-1}. In the face of this variety of estimates we opt, like many previous investigators,[15] to assume $V_j(H^+)$(absolute) = $V_j(H^+)$(conventional) = 0. On this, or any other reasonable, assumption, the partial molar volumes of the complexes $[Fe(CN)_4(bipy)]^{2-}$, $[Fe(CN)_4(phen)]^{2-}$ (phen = 1,10-phenanthroline), and $[Fe(CN)_4L^5]^{2-}$ lie, as expected, between those of $[Fe(CN)_6]^{4-}$ and the respective tris(diimine) complexes, and, again as expected, closer to the former. The dependence of V_j for the ternary complex anions on ligand nature (formulae L^1–L^6) is shown in Fig. 2. In our previous paper on partial molar volumes of iron(II)–diimine complexes[5] we compared such volumes with intrinsic volumes calculated from atom and bond contributions,[16] derived ultimately from the parachor.[17] In view of the problems involved in estimating contributions for transition-metal ions[16,18] and for the metal ion to ligand bonding, and unease in using this approach for charged ternary complexes rather than the simple uncharged organic molecules for which it was designed, we use here relative molecular mass M_r as an empirical measure of intrinsic molecular volume. Fig. 2 shows an approximate correlation between the partial molar volumes of the complex anions and the relative molecular masses of the respective diimine (or diamine) ligands for this series of anionic complexes.

Estimates for the partial molar volume of the $[Fe(CN)_4]^{2-}$ moiety can be obtained in several ways. Reading off V_j(anion) from the plot in Fig. 2 at the M_r of $[Fe(CN)_4]^{2-}$ {*i.e.* estimating the position for the hypothetical $[Fe(CN)_4(L\text{–}L)]^-$ anion with vanishingly small ligand L–L} gives an estimate of approximately $+70$ cm^3 mol^{-1}. Estimates can also be obtained by subtracting the partial molar volumes of the respective ligands, *e.g.* ethane-1,2-diamine (en), bipy or phen, from the values for the complex anions. However this approach does not allow for the fact that the nitrogen-donor atoms of the free ligands will be strongly interacting with water in solution, whereas in the complexes, where they are co-ordinated to a metal ion, they will not. It is preferable to subtract the intrinsic volumes of these ligands, which may be estimated from their densities, whence one obtains estimates close to $+100$ cm^3 mol^{-1}. It is interesting to compare the above estimates for $V_j\{[Fe(CN)_4]^{2-}\}$ with $V_j = +113$ and $+121$ cm^3 mol^{-1} for the complexes $[Zn(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ respectively, derived from published values for their respective potassium salts.[19]

The relation between derived partial molar volumes for the $[Fe(CN)_4(diimine)]^{2-}$ anions and $[Fe(diimine)_3]^{2+}$ cations, and a selection of other inorganic complexes, is shown in Fig. 3. The diagonal line in this figure is the best straight line for the ternary iron(II)–diimine (or diamine)–cyanide complexes, taken from Fig. 2. We can discuss this plot of conventional ionic partial molar volumes *versus* relative molecular mass in absolute terms with confidence so long as we restrict attention to either anions or cations. Comparisons between anions and cations need to be treated with a little caution, especially for

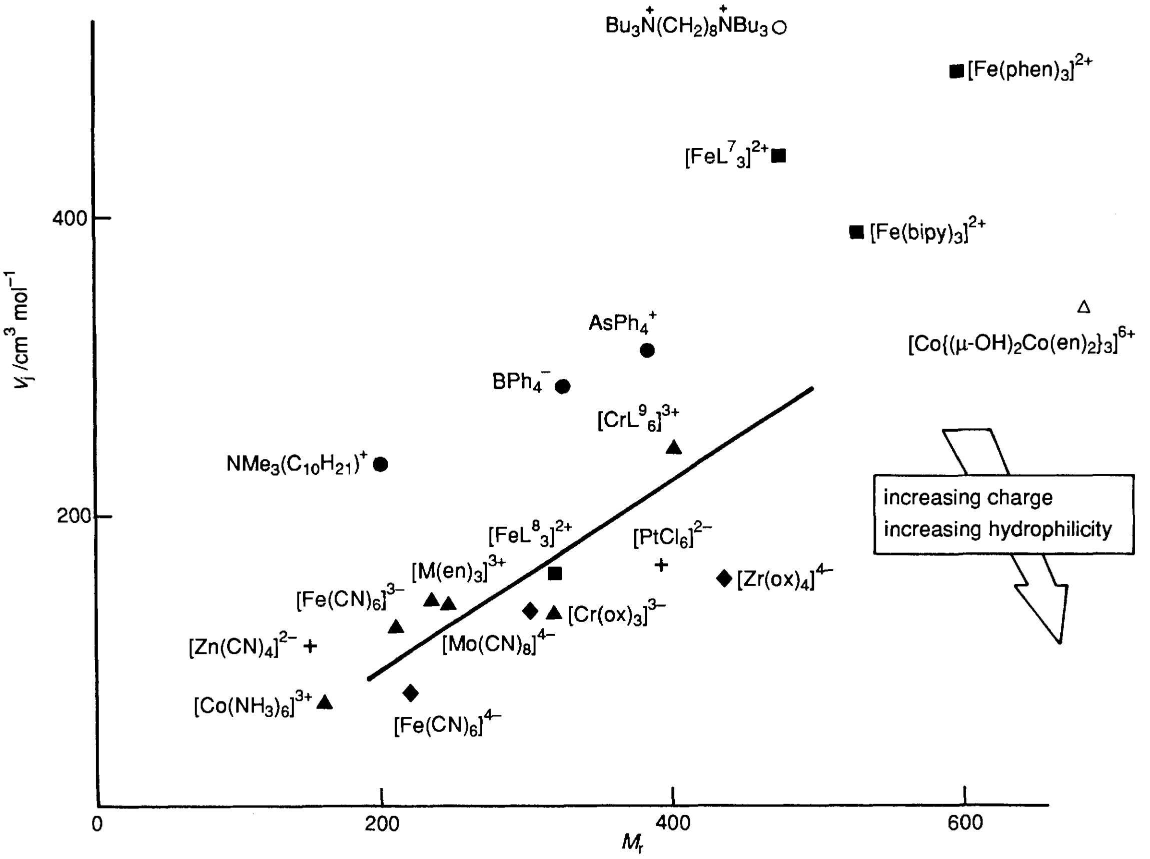


Fig. 3 Relation between partial molar volumes and relative molecular masses for $[Fe(CN)_4(diimine)]^{2-}$ anions (bold diagonal line, from Fig. 2), $[Fe(diimine)_3]^{2+}$ cations (■), a selection of other inorganic complexes (charge 3+ or 3−, ▲; 4−, ◆; 6+, △) and large organic ions (charge 1+ or 1−, ●; 2+, ○). M = Cr or Co; L^9 = urea, ox = oxalate

complexes with relatively high charges. However the uncertainties created by these doubts over absolute values are small compared with the total range of values covered in Fig. 3.

The line for the ternary iron(II)–cyanide–diimine (or diamine) anions in Fig. 3 passes through the centre of the band of points corresponding to the majority of the inorganic complexes, especially the 3+ and 3− ions. The 4− complexes and the large 6+ complex $[Co\{(\mu\text{-}OH)_2Co(en)_2\}_3]^{6+}$ all lie below the line in Fig. 3. Points for hydrophobic organic cations and anions, and for the hydrophobic $[Fe(diimine)_3]^{2+}$ cations (including the $[FeL^5{}_3]^{2+}$ cation, whose high V_j and M_r position is way beyond the right-hand edge of Fig. 3), lie well above this line. Interestingly, the particularly small $[FeL^8{}_3]^{2+}$ cation, whose transfer chemical potential characteristics[20] indicate it to be at the hydrophobic/hydrophilic boundary, lies on the line corresponding to the ternary complexes, which have similar hydrophobic/hydrophilic character.[21] Points for the hydrophobic $AsPh_4^+$, BPh_4^- and $NMe_3(C_{10}H_{21})^+$ (ref. 22) ions lie well above the line for the ternary complexes, like the points for the hydrophobic tris(diimine)iron(II) cations. The points for these species, including the remote $[FeL^5{}_3]^{2+}$ point, lie close to a line parallel to, and about 100 cm^3 mol^{-1} above, the $[Fe(CN)_4(L–L)]^{2-}$ line. The point for the particularly hydrophobic $[Bu_3N(CH_2)_8NBu_3]^{2+}$ cation[1] lies even higher. The contrast between these hydrophobic ions and the hydrophilic 4−, 3−, 3+ (and even 2− for $[PtCl_4]^{2-}$) ions, whose values[1–3,23,24] lie below the trend of the iron(II)–diimine–cyanide complexes, confirms the qualitative pattern of increasing charge or hydrophilicity, in other words of increasing electrostriction, leading to less positive V_j(ion) values. It has been recognised for some time that although groups of similar species, as for example a homologous series, will give good correlations in plots of this type, attempts to expand such correlations to include disparate series of species with rather different solvation characteristics lead to scatter of the type seen in Fig. 3.[25,26]

Our use of relative molecular mass as a rough guide to intrinsic volumes is an approximate approach, which ignores details of geometry that may be of considerable importance. Thus the difference between puckered and planar rings, *e.g.* en *vs.* oxalate, bipy or L^3, may well be significant. The interligand voids in tris(bidentate ligand) complexes containing large planar ligands must play a role in determining solvation; the incorporation of methyl substituents, as in the ligand L^5, may in turn have a significant effect. We[27] are just beginning to explore the calculation of intrinsic volumes and surface areas of complexes, and the relation of solvent geometry to solute geometry, in this context. A combination of such computer modelling with experimental results for a wider range of inorganic complexes should provide a clearer insight into details of solvation and electrostriction, which in turn should greatly help in understanding medium effects on reactivities for substitution and redox reactions of inorganic complexes.[28]

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References

1 F. J. Millero, *Chem. Rev.*, 1971, **71**, 147.
2 A. Indelli and R. Zamboni, *J. Chem. Soc., Faraday Trans. 1*, 1972, 1831.
3 See, for example, G. Wada, E. Nagao, N. Kawamura and K. Kinumoto, *Bull. Chem. Soc. Jpn*, 1978, **51**, 1937; K. Kurotaki and S. Kawamura, *J. Chem. Soc., Faraday Trans. 1*, 1981, 217;

F. Kawaizumi, K. Matsumoto and H. Nomura, *J. Phys. Chem.*, 1983, **87**, 3161; Y. Kitamura, S. Nariyuki and K. Yoshitani, *Inorg. Chem.*, 1985, **24**, 3021.
4 D. A. Palmer and H. Kelm, *Aust. J. Chem.*, 1979, **32**, 1415; M. Kotowski and R. van Eldik, in *Inorganic High Pressure Chemistry*, ed. R. van Eldik, Elsevier, Amsterdam, 1986, ch. 4.
5 M. J. Blandamer, J. Burgess, M. Balon, P. Guardado and A. Maestre, *Transition Met. Chem.*, 1988, **13**, 313.
6 Razak bin Ali, J. Burgess, M. Kotowski and R. van Eldik, *Transition Met. Chem.*, 1987, **12**, 230.
7 A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
8 P. Krumholz, *Struct. Bonding (Berlin)*, 1971, **9**, 139.
9 See, for example, J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1369, 1957.
10 N. J. Blundell, J. Burgess, L. J. S. Prouse and D. R. Russell, unpublished work.
11 O. Redlich and D. M. Meyer, *Chem. Rev.*, 1964, **64**, 221.
12 See, for example, J. Padova, *J. Chem. Phys.*, 1963, **39**, 1552; Y. Kitamura, R. van Eldik and H. Kelm, *Inorg. Chem.*, 1984, **23**, 2038 and refs. therein.
13 H. D. B. Jenkins and M. S. F. Pritchett, *Philos. Mag. B*, 1983, **48**, 493.
14 See, for example, Y. Marcus, *Ion Solvation*, Wiley, New York, 1985; O. Popovych, *Crit. Rev. Anal. Chem.*, 1970, **1**, 73.
15 See, for example, M. J. Sisley and T. W. Swaddle, *Inorg. Chem.*, 1981, **20**, 2799 and refs. therein.
16 J. C. McGowan and A. Mellors, *Molecular Volumes in Chemistry and Biology*, Ellis Horwood, Chichester, 1986, ch. 2.
17 S. Sugden, *The Parachor and Valency*, Routledge, London, 1929.
18 J. C. McGowan, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 193.
19 J. G. Mathieson and G. Curtnoys, *J. Chem. Soc., Faraday Trans. 1*, 1975, 1114.
20 M. J. Blandamer and J. Burgess, *Transition Met. Chem.*, 1988, **13**, 1.
21 J. Burgess, S. Radulovic and F. Sanchez, *Transition Met. Chem.*, 1987, **12**, 529.
22 R. de Lisi, S. Milioto and R. Triolo, *J. Solution Chem.*, 1989, **18**, 905.
23 K. Yoshitani, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2327.
24 G. A. Bottomley, L. G. Glossop and W. P. Staunton, *Aust. J. Chem.*, 1979, **32**, 699.
25 F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, 1968, **72**, 1758.
26 B. E. Conway, R. E. Verrall and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738.
27 J. Burgess, P. Guardado, C. D. Hubbard and D. M. P. Mingos, unpublished work.
28 J. Burgess and E. Pelizzetti, *Gazz. Chim. Ital.*, 1988, **118**, 803.

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