Letters

A disagreement between measured equilibrium constants for ligand–ligand substitution and disproportionation processes in mixed mercury(II) dihalides

A number of equilibrium constants for mixed mercury(II) dihalides, HgXY, reported by Griffiths and Anderson [1,2] differ considerably from those we have determined.[3-9]

The equilibrium constants of the processes (1) [2-5] and (2) [2,6-8]

$$HgX_2 + Y^- \rightleftharpoons HgXY + X^- \; (\log_{10}\beta_1') \qquad (1)$$

$$HgX_2 + HgY_2 \rightleftharpoons 2HgXY \; (\log_{10}K) \qquad (2)$$

can easily be compared on the basis of a cycle and the equilibrium constants of processes (3). Values of $\log_{10}\beta_2$ can be

$$Hg^{2+} + 2X^-(Y^-) \rightleftharpoons HgX_2(HgY_2) \; (\log_{10}\beta_2) \qquad (3)$$

obtained from collected information,[10] *i.e.* $\log_{10}\beta_2 = 14.18$ (Cl^-), 18.39 (Br^-), and 25.10 (I^-) at $T = 20$ °C and $I \longrightarrow 0$ mol dm^{-3}. We also determined values of $\log_{10}\beta_2$ independently, which are in a good agreement, and which we have used. Comparison of values of $\log_{10}\beta_1'$ determined experimentally with those derived from the combination of $\log_{10}K$ and $\log_{10}\beta_2$ are presented in the Table. A large disagreement between the data obtained by Griffiths and Anderson can be observed, whereas, in contrast our results are in excellent agreement. We consider our data to be correct and that a number of the data of Griffiths and Anderson are considerably distorted.

Table. Values of $\log_{10}\beta_1'$ at 20 °C and $I \longrightarrow 0$ mol dm^{-3}

	Data of Griffiths and Anderson [2]		Our data [3-8]	
HgXY	Experimental	From combination of $\log_{10}K$ with $\log_{10}\beta_2$	Experimental	From combination of $\log_{10}K$ with $\log_{10}\beta_2$
HgClI	0.98 ± 0.05	6.16	5.77 ± 0.03 5.83 ± 0.03*	5.88
HgBrI	0.52 ± 0.09	3.98	3.68 ± 0.03*	3.64
HgBrCl	0.23 ± 0.09	2.46	2.37 ± 0.05	2.46

* Results recalculated to 20 °C.

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Griffiths and Anderson reply. Belevantsev and Shoovayev have rightly pointed out that the equilibrium constants for the formation of HgXY determined by us [1,2] (we have used their reference numbers) and by them [3-9] are different. The reasons are interesting.

They employed established stability constants,[10] which were generally determined around 1949, and state that they have also obtained independently data in good agreement. The techniques used, however, often involved traditional analyses of saturated solutions, with no specific procedure for identifying that only the species discussed were indeed present. Our technique, employing digitised spectra of solutions of 10^{-3} mol dm^{-3} and less, permitted us to calculate by more than one independent method the *spectra* of the various HgXY species using multiple linear regressional analysis. Once the spectra were established as unique, then the concentrations in the various solutions were determined, and hence the equilibrium constants. This is a new approach and eliminates problems that can arise from constants determined from absorption data recorded at a few selected wavelengths. Our procedure is thus self consistent, and our error limits are our estimates based on possible variations in the recorded spectra, and not the calculated standard deviations, which were considerably less.

Belevantsev and Shoovayev always include consideration of hydrolysis and the reaction $HgX_2 \rightleftharpoons HgX^+ + X^-$, but under our experimental conditions we were unable to find any evidence of these reactions occurring. Thus their assumption that these reactions must be included in determining HgXY equilibrium constants contributes to the observed discrepancy between our data and theirs. Further, since they have informed us (in correspondence) that our calculated mixed-halide spectra agree with theirs, then the difference in the equilibrium constants must arise from assumptions made in the calculation procedures.

We are reluctant to agree that the magnitude of the differences (Table) provides a 'large disagreement'. We do not accept that our results 'are considerably distorted,' since our computer programs gave very acceptable residual and regression sums of squares, *F* ratios, multiple correlation coefficients, and degrees of freedom of the *F* ratio.[1]

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Evidence for *cis* effects in carbonyl complexes of bis(dimethylglyoximato)iron(II)

In their paper on $[Fe(Hdmg)_2L(CO)]$ and $[Fe(Hdmg)_2L_2]$ (H_2dmg = dimethylglyoxime, L = pyridine or 1-methylimidazole), Sams and co-workers[1] infer that *cis* effects are evidenced by changes in the asymmetric parameter η obtained from Mössbauer data. This conclusion should be received with caution because a change in η could be observed in the absence of any *cis* effect.

The valence contribution to the electric field gradient (e.f.g.) tensor components can be expressed in terms of the effective populations n_i of the iron 3*d* orbitals by equations (1)—(3), where k is a constant, *ca.* 3 mm s^{-1}.[2] Let us suppose,

$$v_{xx} = k[\tfrac{1}{2}(n_{z^2} - n_{x^2-y^2}) + n_{yz} - \tfrac{1}{2}(n_{zx} + n_{xy})] \quad (1)$$

$$v_{yy} = k[\tfrac{1}{2}(n_{z^2} - n_{x^2-y^2}) + n_{zx} - \tfrac{1}{2}(n_{xy} + n_{yz})] \quad (2)$$

$$v_{zz} = k[n_{x^2-y^2} - n_{z^2} + n_{xy} - \tfrac{1}{2}(n_{yz} + n_{zx})] \quad (3)$$

for example, cases 1 and 2 with n_i values as shown in the Table. Then, by assuming k = 3 mm s^{-1}, the e.f.g. tensor components calculated are in complete agreement with those determined experimentally for $[Fe(Hdmg)_2(py)_2]$ and $[Fe(Hdmg)_2(py)(CO)]$ (η = 0.73 for case 1 and 0.55 for case 2, regardless of the numerical value of k). The values of n_{z^2}, n_{yz}, and n_{zx} in case 2 are different from those in case 1; the two cases correspond to complexes with different axial ligands. On the other hand, $n_{x^2-y^2}$ and n_{xy} are the same in cases 1 and 2: any *cis* effect is not considered. It would therefore seem premature to conclude that a change in η is evidence for *cis* effects.

Table. Effective populations of iron 3*d* orbitals

Case	$n_{x^2-y^2}$	n_{z^2}	n_{xy}	n_{yz}	n_{zx}
1	0.53	0.16	1.99	1.97	1.71
2	0.53	0.45	1.99	1.77	1.62

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