The Kinetics of Formation of Ternary Complexes between Substituted Copper(II) Species and the Bidentate Ligand Pyridine-2-azo-*p*-dimethylaniline

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Summary The rate constants for the formation and dissociation of ternary complexes of Cu^{II} with pyridine-2-azo-*p*-dimethylaniline (pada) in water depend on the relative positions of replaceable water molecules.

THE pattern of 1 : 1 complex formation involving labile metal ions has become well-established.[1] The rate constant for formation k_f depends primarily on the nature of the metal, so that reactions between a given metal and most ligands of the same charge-type have approximately the same value of k_f; the variation in equilibrium constant K is usually reflected in differences in the dissociation rate constant k_d. Deviations from this pattern have been reported in which the values of k_f for chelating ligands are either lower or higher than usual because of, respectively, the rate-limiting closure of the chelate ring[2] and the involvement of an internal conjugate base mechanism.[3] The effects of bound ligands on the kinetics of replacement of further solvent molecules have been much less widely reported, despite the importance of the resulting ternary complexes in enzymatic and other catalytic situations. We report the kinetics, as measured by the temperature-jump relaxation method, of the reaction between pyridine-2-azo-*p*-dimethylaniline (pada) and Cu^{II} species in which the rates are very significantly reduced, apparently by the necessity of bound groups at the metal ion to move in order to accommodate the second group on the incoming ligand.

pada is a bidentate ligand which binds through two N atoms. It is apparently "normal" in the sense used above, even with very labile metals such as Cu^{II}.[1,3,4] The lability of Cu^{II} is thought to be associated primarily with the loosely-held axial water molecules, and the dynamic Jahn–Teller effect[5] permits a rapid shift in the co-ordinate axes on replacement of the first H_2O.

It will be seen (Table) that this picture is not significantly affected by bound groups as long as there are still two H_2O molecules in the *cis*-position [in †$Cu(en)(H_2O)_4^{2+}$, $Cu(bipy)(H_2O)_4^{2+}$, and $Cu(dien)(H_2O)_3^{2+}$]. The case of $Cu(bipy)_2(H_2O)_2^{2+}$ is interesting in that it has been shown[6] that the two H_2O molecules are in the *cis*-position, presumably because of steric interference between the two aromatic ring systems (the fact that k_f is reduced by an order of magnitude is not surprising in view of the probable steric hindrance between the bipy rings and the ring of pada). However, when the replaceable water molecules are in the

Rate constants[a] *for complex formation* (25°)

	k_f(1 $mole^{-1}$ s^{-1})	k_d(s^{-1})
$Cu(H_2O)_6^{2+}$ + pada ..	1×10^{8} [b]	1×10^{3} [b]
Cu $en(H_2O)_4^{2+}$ + pada ..	*ca.* 5×10^{8}	*ca.* 1×10^{4}
$Cu(bipy)(H_2O)_4^{2+}$ + pada	$>10^{8}$	—
$Cu(dien)(H_2O)_3^{2+}$ + pada	$2{\cdot}0 \times 10^{8}$	$5{\cdot}0 \times 10^{4}$
$Cu(bipy)_2(H_2O)_2^{2+}$ + pada	*ca.* 3×10^{7}	—
$Cu(en)_2(H_2O)_2^{2+}$ + pada ..	$3{\cdot}9 \times 10^{5}$	*ca.* 5
$Cu(gly)_2(H_2O)_2^{2+}$ + pada ..	$1{\cdot}5 \times 10^{6}$	$5{\cdot}4 \times 10^{2}$

[a] Values of k_f have been adjusted to take account of the reduced number of available water molecules in CuL species (see ref. 10).

[b] Data from R. G. Wilkins, *Inorg. Chem.*, 1964, **3**, 520 (at 15°).

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† Abbreviations used are bipy: 2,2′-bipyridyl; en: ethylenediamine; dien: diethylenetriamine; gly:glycine.

trans-configuration [as with $Cu(en)_2(H_2O)_2^{2+}$ (ref. 7) and $Cu(gly)_2(H_2O)_2^{2+}$ (ref. 8)] there is a large reduction in k_f which we attribute to the rate-determining reorganisation of the metal complex, involving the movement of one bound group of en or gly from the equatorial to the axial position. The effect is also found in k_d so that, although there is a certain variation in K along the series, it is considerably smaller than that in k_f and k_d. (In fact, the variations in K are greater than those observed for Zn^{II}[4] and Co^{II}[9] with pada or with Mg^{II}[10] and Mn^{II}[11] with a comparable bidentate ligand, 8-hydroxyquinoline). Further details of our assignments, together with the activation parameters for these and related systems, will be published elsewhere.

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