Slow Substitution Reactions of the Copper Complex of 2,2′,2″-Triaminotriethylamine

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Summary The substitution reactions of Cu^{II} complexes proceed relatively slowly in the absence of Jahn–Teller distortions.

THE substitution reactions of $[Cu(H_2O)_6]^{2+}$ and its complexes with several ligands appear to follow the fairly well established mechanism for complex formation involving bivalent metal ions in aqueous solution,[1–3] with the large rate constants for complex formation being explained in terms of a rate-determining substitution into the axial co-ordination position of the metal complex followed by rapid Jahn–Teller inversion to give the final product.[4] Previous work on the reaction of substituted copper species with the bidentate ligand pada†[5] has shown that co-ordinated ligands do not significantly alter the substitution properties of $[Cu(H_2O)_6]^{2+}$ provided that there are two water molecules in a *cis*-configuration in the reacting complex. If, however, the remaining water molecules are in a *trans*-arrangement then there is a large reduction in the size of the formation rate constant, k_f, for bidentate ligands attributable to the rate-determining re-organization of the metal complex.

TABLE. Formation rate constants for substitution reactions of Cu^{II} complexes (25 °C).

		k_f/l mol^{-1} s^{-1}	k_d/s^{-1}	Ref.
$[Cu(H_2O)_6]^{2+}$	+ imidazole	$5{\cdot}7 \times 10^{8}$	$2{\cdot}6 \times 10^{4}$	9
$[Cu(tren)(H_2O)]^{2+}$	+ pyridine	$1{\cdot}6 \times 10^{5}$	$1{\cdot}7 \times 10^{3}$	a
$[Cu(tren)(H_2O)]^{2+}$	+ 3-methylpyridine	$1{\cdot}8 \times 10^{5}$	$9{\cdot}4 \times 10^{2}$	a
$[Cu(tren)(H_2O)]^{2+}$	+ 4-methylpyridine	$2{\cdot}4 \times 10^{5}$	$8{\cdot}0 \times 10^{2}$	a
$[Cu(tren)(H_2O)]^{2+}$	+ imidazole	*ca.* $2{\cdot}0 \times 10^{5}$	*ca.* 150	a
$[Cu(tren)(H_2O)]^{2+}$	+ H_2O	$2{\cdot}5 \times 10^{5}$[b]	—	8
$[Cu(en)(H_2O)_4]^{2+}$	+ pada[c]	*ca* $3{\cdot}5 \times 10^{8}$	*ca.* $1{\cdot}0 \times 10^{4}$	4
$[Cu(dien)(H_2O)_3]^{2+}$	+ pada[c]	$1{\cdot}0 \times 10^{8}$	$5{\cdot}0 \times 10^{4}$	4

[a] This work. [b] First order rate constant, units s^{-1}. [c] Rate constants from ref. 4 have been converted to overall rate constants rather than statistically adjusted constants as reported.

In this communication we report the kinetics of reaction of a series of monodentate ligands with the copper complex of 2,2′,2″-triaminotriethylamine $[Cu(tren)H_2O]^{2+}$. The crystal structure of $[Cu(tren)NCS]^{+}SCN^{-}$ shows the complex to be trigonal bipyramidal with a relatively short Cu–NCS bond length.[6] For the aquo-complex the low pK_a value for the co-ordinated water molecule,[7] the detection by n.m.r. spectroscopy[8] of only one relatively small rate constant, $k(M–H_2O)$, for solvent exchange, and the ability to form only the one complex with monodentate ligands, suggests that the five co-ordinate trigonal bipyramidal structure is maintained.

The presence of tren in the inner co-ordination sphere of Cu^{II} has a dramatic effect on the rate of substitution at the copper centre, reducing the formation rate constants by a factor of *ca.* 3000 compared to similar reactions with $[Cu(H_2O)_6]^{2+}$. The dissociation rate constants, k_d, are also reduced to a similar extent so that the stability of the ternary complexes parallels that of the same ligands reacting with Cu^{2+} (aq.). The ratios of $k_f/k(M–H_2O)(K_{os})$ ranging from 0·6 to 1·0 l mol^{-1} are slightly larger than normally found for neutral ligands reacting with a bivalent metal ion; however, the lack of dependence of the formation rate constants on the nature of the incoming ligand suggests that the usual mechanism for substitution at a labile metal centre is operating.

The large decrease in k_f for $[Cu(tren)H_2O]^{2+}$ compared to $[Cu(H_2O)_6]^{2+}$ cannot be attributed *per se* to the presence of nitrogen donor ligands in the inner co-ordination sphere of the copper as a similar decrease in k_f is not seen for the reaction of pada with $[Cu(dien)(H_2O)_3]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$.[5] Again, a reduction in k_f due to nitrogen donor ligands would be in marked contrast to the reactions of Ni^{II} [10–13] and Co^{II} [12] where the presence of co-ordinated nitrogen ligands causes a marked increase in the rate of ligand substitution and solvent exchange. A small decrease in the formation rate constant compared to $[Cu(H_2O)_6]^{2+}$ would be expected because the change in the crystal field stabilization energy for the formation of the reaction intermediate is different for the trigonal bipyramidal and octahedral complexes. However, the most important single factor in determining the value of $k(M–H_2O)$ is the strength of the bond between the metal atom and the co-ordinated water molecule and only part of this bond energy is related to crystal field effects.[14]

The results are consistent with a slow solvent exchange process determined by the geometry of the complex which requires the displacement of an 'equatorial-like' water without the assistance of any Jahn–Teller inversion. The absence of Jahn–Teller effects brings the water exchange rate constant in line with those for other metal ions of comparable radius {*e.g.* $[Co(H_2O)_6]^{2+} + NH_3$; $k_f = 1{\cdot}1 \times 10^{5}$ l mol^{-1} s^{-1} (ref. 15)}. Attempts to confirm this interpretation by measuring the substitution rate constants on the square pyramidal copper trien complex[16] were unsuccessful because the low stability of the adducts in the axial position requires the use of high reactant concentrations to produce any product and puts the observed rate constants outside the range of the temperature-jump instrument. This also makes the estimation of a lower limit for the formation rate constant unreliable.

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† Abbreviations used are: pada: pyridine-2-azo-*p*-dimethylaniline; dien: diethylenetriamine; trien: triethylenetetramine; en: ethylenediamine.

The importance of slow substitution reactions at the metal centre in the catalytic mechanism of copper proteins is becoming increasingly apparent.[17] The present study suggests that this may be due to the specific geometry of the copper centre.

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[1] M. Eigen and R. G. Wilkins, 'Mechanisms of Inorganic Reactions,' ed. R. F. Gould, Adv. Chem. Series No. 29 (Amer. Chem. Soc., Washington, D.C., 1965), p. 55.

[2] D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

[3] T. S. Roche and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1974, **96**, 5082.

[4] M. Eigen, *Ber. Bunsenges. Phys. Chem.*, 1963, **67**, 753.

[5] M. A. Cobb and D. N. Hague, *Chem. Comm.*, 1971, 192.

[6] P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 6131.

[7] P. Paoletti and M. Ciampolini, *Ricerca Sci. series A*, 1963, **3**, 399.

[8] D. P. Rablen, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1972, **94**, 1771.

[9] H. Diebler and Ph. Rosen, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 1031.

[10] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 1088.

[11] J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 1875.

[12] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

[13] D. F. Rablen, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1976, **15**, 931.

[14] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd edn., Wiley, New York, 1967.

[15] D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.

[16] G. Marongiu, E. C. Lingafelter, and P. Paoletti, *Inorg. Chem.*, 1969, **8**, 2763.

[17] B. J. Marwedal, R. J. Kurland, D. J. Kosman, and M. J. Ettinger, *Biochem. Biophys. Res. Comm.*, 1975, **63**, 773; R. W. Barker, N. Boden, G. Cayley, S. C. Charlton, R. Henson, M. C. Holmes, I. Kelly, and P. F. Knowles, unpublished work.