Dissociation of Aqua[tris(2-dimethylaminoethyl)amine-*NN′N″N‴*]-cobalt(II) and its Nickel(II) and Copper(II) Analogues in Perchloric Acid Solution

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A stopped-flow spectrophotometric study of the dissociation of five-co-ordinate $[Co(tda)H_2O]^{2+}$ [tda = tris-(2-dimethylaminoethyl)amine] and the nickel(II) and copper(II) analogues in acidic 2·0M-ClO_4^- aqueous solution is reported. A single process has been observed for all three metal complexes and is attributed to the dissociation of the first amine group. Kinetic parameters for the cobalt(II), nickel(II), and copper(II) complexes respectively are: k(293 K) = 0·97 ± 0·01 s^{-1}, $\Delta H^{\ddagger}$ = 61·9 ± 2·9 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −33·5 ± 9·8 J K^{-1} mol^{-1}; 7·87 ± 0·04 s^{-1}, 58·9 ± 1·3 kJ mol^{-1}, −26·4 ± 4·6 J K^{-1} mol^{-1}; and 28·0 ± 0·8 s^{-1}, 81·1 ± 2·5 kJ mol^{-1}, 59·9 ± 8·4 J K^{-1} mol^{-1}. Possible sources of the variations in the magnitudes of these parameters are discussed in terms of both dissociative and associative reaction mechanisms.

THE structural, spectroscopic, and thermodynamic aspects of multidentate amine five-co-ordinate complexes of the bivalent first-row transition-metal ions are currently the subject of much interest,[1-5] but only limited information on the kinetic characteristics of these complexes is available.[6-8] In studies of the dissociation of multidentate amine ligands from six-co-ordinate metal complexes, several steps in the unwrapping of the amine

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[1] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

[2] M. Ciampolini, *Structure and Bonding*, 1969, **6**, 52.

[3] P. Paoletti and M. Ciampolini, *Inorg. Chem.*, 1967, **6**, 64.

[4] M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.

[5] M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5**, 45.

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

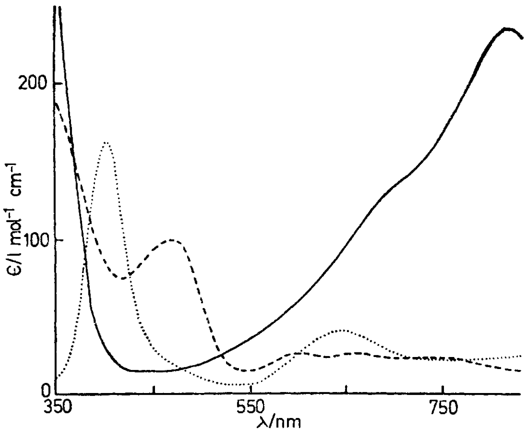
[7] R. J. West and S. F. Lincoln, *Inorg. Chem.*, 1973, **12**, 494, 3021.

[8] R. J. West and S. F. Lincoln, *J.C.S. Dalton*, 1974, 281.

have been detected and kinetically characterised.[9-11] In the case of a five-co-ordinate complex, the first step in the process of dissociation of the multidentate amine from the metal ion will be characteristic of that co-ordination state. Accordingly the kinetics of dissociation of tris(2-dimethylaminoethyl)amine (tda) from five-co-ordinate $[Co(tda)H_2O]^{2+}$ and its nickel(II) and copper(II) analogues [4] have been studied.

RESULTS AND DISCUSSION

The visible spectra in the Figure are those obtained from solutions of $[M(tda)ClO_4][ClO_4]$ in 2·0M-aqueous sodium perchlorate at the pH assumed by the solutions on dissolution of each of the three complexes (M = Co, Ni, and Cu).* These spectra are considered to typify $[M(tda)H_2O]^{2+}$, the product of rapid aquation of the perchlorato-complex. The presence of the single aqua-ligand was demonstrated by potentiometric-titration studies,[12] and isolation of $[Cu(tda)H_2O][ClO_4]_2$ from solution has been reported.[13] The spectral envelopes and magnitudes of the absorption coefficients in the Figure are as anticipated for high-spin systems in a C_{3v} field [2] {as exemplified by published [4] spectra for a range of $[M(tda)X]^+$ species (X = Cl, Br, I, NO_3, or ClO_4)} and there is little doubt that they characterise the aqua-analogues of the $[M(tda)Br]^+$ series, for which *X*-ray determinations show trigonal-bipyramidal structures.[14,15]



Visible spectra of: (· · · ·), $[Ni(tda)H_2O]^{2+}$ (pH 7·72); (— — —), $[Co(tda)H_2O]^{2+}$ (pH 7·55); and (——), $[Cu(tda)H_2O]^{2+}$ (pH 6·65) in 2·0M-aqueous sodium perchlorate solution at 298 K

At an ionic strength adjusted to 2·0M with sodium perchlorate, $[M(tda)H_2O]^{2+}$, stable at neutral pH, dissociated rapidly in acid solution to produce visible spectra consistent with those reported for the appropriate hexa-aqua-ions. For each metal ion a single kinetic process was observed over the ranges of acid and metal-complex concentrations at the several wavelengths studied, and was characterised by optical-density changes within 10% of that anticipated from the absorption-coefficient difference between that of the hexa-aqua-ion [16] and its

TABLE 1

Dissociation of $[M(tda)H_2O]^{2+}$ in perchloric acid at 2·0M ionic strength adjusted with sodium perchlorate

Complex [a]	*T*/K	$[HClO_4]$/M	k [b]/s^{-1}	λ/nm
$[Co(tda)H_2O]^{2+}$	303·0	0·025	2·56	470
		0·050	2·60	470
		0·10	2·49	470
		0·20	2·38	470
		0·40	2·46	470
		0·60	2·28	470
		0·80	2·30	470
		1·00	2·40	470
		1·00	2·50 [c]	470
		1·00	2·48 [c]	410
		1·00	2·47 [c]	510
		1·00	2·60 [c]	610
		1·00	2·58 [c]	700
	293·0	1·00	0·972	470
	298·0	1·00	1·36	470
	308·0	1·00	3·56	470
	313·0	1·00	4·96	470
$[Ni(tda)H_2O]^{2+}$	293·0	0·025	5·50	470
		0·050	5·98	470
		0·10	6·47	470
		0·20	7·68	470
		0·40	7·65	470
		0·60	7·41	470
		0·80	7·74	470
		1·00	7·87	470
		1·00	7·08 [d]	470
		1·00	7·70 [c]	470
		1·00	7·73 [c]	370
		1·00	7·95 [c]	450
		1·00	7·81 [c]	600
		1·00	7·93 [c]	650
		1·00	7·90 [c]	700
	273·2	1·00	1·22	470
	278·0	1·00	1·84	470
	282·9	1·00	2·75	470
	288·0	1·00	4·86	470
	297·9	1·00	11·3	470
	303·0	1·00	16·9	470
$[Cu(tda)H_2O]^{2+}$	293·0	0·025	25·0	660
		0·050	29·0	660
		0·10	27·8	660
		0·20	28·4	660
		0·40	29·1	660
		0·60	28·2	660
		0·80	28·0	660
		1·00	28·0	660
		1·00	27·8	640
	273·2	1·00	2·31	660
	280·0	1·00	5·63	660
	286·0	1·00	11·1	660
		1·00	10·9 [c]	660
		1·00	11·0 [c]	370
		1·00	10·7 [c]	700

[a] $[Complex]_0 = 1 \times 10^{-3}$M. [b] The average of at least five runs, the variance of which never exceeded ±3%. [c] $[Complex]_0 = 5{\cdot}0 \times 10^{-3}$M. [d] $[Complex]_0 = 2{\cdot}0 \times 10^{-3}$M.

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* 1M = 1 mol dm^{-3}.

[9] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 1963, 2662.

[10] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.

[11] S. J. Ranney and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 2437.

[12] J. H. Coates, G. J. Gentle, and S. F. Lincoln, *Nature*, 1974, **249**, 773; in 1·0M-aqueous sodium perchlorate the pK_a (298 K) of the aqua-ligand in $[M(tda)H_2O]^{2+}$ is 8·80, 9·53, and 8·52 when M = Co, Ni, and Cu respectively.

[13] A. Cristini and G. Ponticelli, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2691.

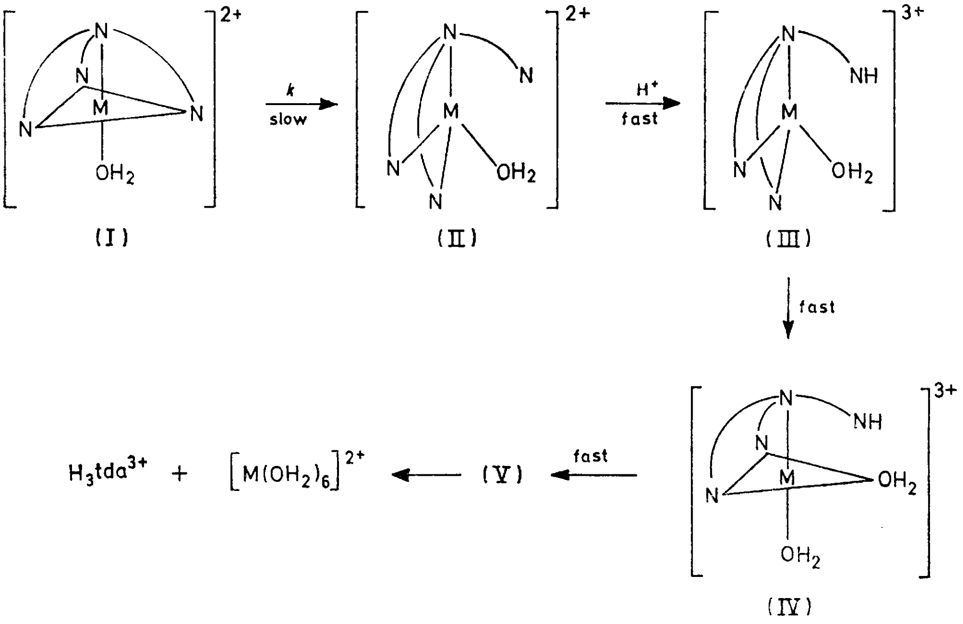
[14] M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 955; in this study the determined distances were Co–N (apical) = 2·151 ± 0·021, Co–N (equatorial) = 2·080 ± 0·018, and Co–Br = 2·431 ± 0·004 Å.

[15] M. Di Vaira and P. L. Orioli, *Acta Cryst.*, 1968, **B24**, 595; in this study the determined distances were Ni–N (apical) = 2·10 ± 0·01, Ni–N (equatorial) = 2·13 ± 0·01, Ni–Br = 2·467 ± 0·002, Cu–N (apical) = 2·07 ± 0·01, Cu–N (equatorial) = 2·14 ± 0·01, and Cu–Br = 2·393 ± 0·003 Å.

[16] B. N. Figgis in 'Introduction to Ligand Fields,' Interscience, New York, 1966, ch. 9.

$[M(tda)H_2O]^{2+}$ precursor. The first-order dissociation rate constant, *k*, for $[Ni(tda)H_2O]^{2+}$ exhibited a dependence on acid concentration in the low concentration range, but attained a constant value above 0·2M-acid, as was also observed for dissociation of multidentate amines from six-co-ordinate nickel(II) species.[9] The dissociation of the cobalt(II) and copper(II) species exhibited a constant *k* value over the acid concentration range (Table 1), which implies that the p*K* of the free amine group [species (II) in the Scheme] is higher for these two metal ions than is the case for nickel(II). In the ensuing discussion, *k* values at 1·0M-acid are used for comparative purposes.

The magnitude of the optical-density changes, and the acid-concentration and wavelength independence of *k*, indicate that dissociation of the first of the three equivalent amine groups of tda is the rate-determining step for the observed kinetic process. In a dissociative mechanism (Scheme) the first product, (II), must be four-co-ordinate and may tend towards the tetrahedral geometry assumed by all three metal ions with some other ligands.[17] The subsequent fast protonation is necessary to rationalise the acid independence of *k*, and is consistent with a generally accepted mechanism for dissociation of metal chelate complexes.[18] The co-ordination number of M prior to dissociation of the second amine group is not established, but the postulated species (IV) is a plausible intermediate as it closely resembles the well established $[M(bdma)X_2]$ species {bdma = bis[(2-dimethylamino)ethyl]methylamine; X = halide; M = Co, Ni, and Cu} [5] in its approximate trigonal-bipyramidal structure and donor-atom set. Species (IV) should exhibit similar absorption coefficients to (I), but at different wavelengths as a consequence of the change in donor-atom set. It is probable that the products, (V), of dissociation of the second NMe_2 group from M will be six-co-ordinate. Cobalt(II) [19] and nickel(II) [9] six-co-ordinate multidentate amine complexes almost invariably exhibit absorption coefficients less than 20 l mol^{-1} cm^{-1} in the visible region, but this is not necessarily the case for copper(II).[20] The observation of only one kinetic process infers that all species characterised by absorption coefficients comparable to those of $[M(tda)H_2O]^{2+}$ dissociate more rapidly than their precursor $[M(tda)H_2O]^{2+}$, and that either a similar constraint applies to species with smaller absorption coefficients, or their absorption coefficients are very similar to the hexa-aqua-species and their reactions are consequently not detected.



SCHEME

The order of lability (298 K) exhibited for the dissociation of $[M(tda)H_2O]^{2+}$ ($Cu^{2+} > Ni^{2+} > Co^{2+}$) contrasts with that observed in six-co-ordinate systems ($Cu^{2+} > Co^{2+} > Ni^{2+}$), and similarly the relatively high $\Delta H^{\ddagger}$ value (Table 2) for $[Cu(tda)H_2O]^{2+}$ contrasts with the six-co-ordinate state in which $\Delta H^{\ddagger}$ is expected to vary as $Cu^{2+} < Co^{2+} < Ni^{2+}$.[18,20,21] These contrasts must be largely attributed to the change from six- to five-co-ordination and the consequent modification of the *d*-orbital energies,[18] and also to variations in metal–ligand distances within the $[M(tda)H_2O]^{2+}$ series which, by

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[17] F. A. Cotton and G. Wilkinson in 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, ch. 25.

[18] F. Basolo and R. G. Pearson in 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 218 and chs. 2—3.

[19] P. Paoletti, M. Ciampolini, and S. Sacconi, *J. Chem. Soc.*, 1963, 3589.

[20] R. G. Wilkins, *J. Chem. Soc.*, 1962, 4475.

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

analogy with $[M(tda)Br]^+$, is assumed to possess trigonal-bipyramidal geometry.[1,14,15] If dissociation of the first amine group [(I) ⟶ (II)] proceeds through an approximately tetrahedral transition state, the appropriate crystal-field activation energies (c.f.a.e.) are 0·10, 2·70, and 5·30 *Dq* respectively for high-spin cobalt(II), nickel(II), and copper(II).[18] Undoubtedly the dissimilarity of the ligand donor groups and the uncertainties involved in crystal-field calculations must make these c.f.a.e. values highly qualitative in nature; nevertheless it is noteworthy that the highest c.f.a.e. is that of copper(II), which also exhibits the greatest $\Delta H^\ddagger$ value. The M–N (equatorial), M–N (apical), and M–Br distances all show considerable variation as M varies in $[M(tda)Br]^+$ as a net consequence of *d*-orbital occupancy and ligand steric restrictions.[1] Similar bonding-distance variations are to be expected in $[M(tda)H_2O]^{2+}$ with a resultant variation in the ring strain in the tda ligand, and as there is substantial evidence that increases in ring strain decrease [10,11] $\Delta H^\ddagger$ (see Table 2), it is probable that some of the variation in $\Delta H^\ddagger$ observed in this study may be attributed to this source.

TABLE 2

Activation parameters for the dissociation of $[M(tda)H_2O]^{2+}$ in 1·0M-perchloric acid at 2·0M ionic strength adjusted with sodium perchlorate

Complex	k(293 K)/ s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K mol^{-1}
$[Co(tda)H_2O]^{2+}$	0·97 ±0·01	61·9 ±2·9	−33·5 ±9·8
$[Ni(tda)H_2O]^{2+}$	7·87 ±0·04	58·9 ±1·3	−26·4 ±4·6
$[Cu(tda)H_2O]^{2+}$	28·0 ±0·8	81·1 ±2·5	59·9 ±8·4
$[Ni(en)(H_2O)_4]^{2+}$ *	0·15	83·2	18·7
$[Ni(pt)(H_2O)_3]^{2+}$ *	63	71·9	30·9
$[Ni(3NH\text{-}pd)(H_2O)_3]^{2+}$ *	14	72·3	19·9
$[Ni(4NH\text{-}hd)(H_2O)_3]^{2+}$ *	11	71·9	16·5
$[Ni(taa)(H_2O)_2]^{2+}$ *	66	56·5	−20·5
$[Ni(3,6NH\text{-}od)(H_2O)_2]^{2+}$ *	15	59·4	−23·0

* Activation parameters calculated from data for the dissociation of the first amine group given in ref. 9, where the *k* values refer to 298 K. Melson and Wilkins drew attention to the decrease in $\Delta H^\ddagger$ as ring strain increases in the order bidentate diamine < tridentate triamine < quadridentate tetramine. en = Ethylenediamine, pt = propane-1,2,3-triamine, 3NH-pd = 3-azapentane-1,5-diamine, 4NH-hd = 4-azaheptane-2,6-diamine, taa = tris(2-aminoethyl)amine, and 3,6NH-od = 3,6-diazaoctane-1,8-diamine.

The alternative mechanism to that so far discussed is an associative mechanism in which a second water molecule is co-ordinated to give a five-co-ordinate product [species (II) with an additional water molecule co-ordinated] from a six co-ordinate associative transition state. If this transition state approximates to an octahedron, then the c.f.a.e. contributions involved are −2·56, −5·74, and 1·08 *Dq* for cobalt(II), nickel(II), and copper(II) respectively. Once again these results must be considered highly qualitative, but it is interesting that copper(II) has a significant c.f.a.e. contribution whilst those of the other ions are effectively zero.[22] A distinction between these two extreme mechanisms is not readily made, and in any case the variation of the $\Delta S^\ddagger$ data suggests that the involvement of water in the transition state and the geometry of that state may vary with the metal ion to some extent.

The order of lability and relative magnitudes of $\Delta H^\ddagger$ observed for the $[M(tda)H_2O]^{2+}$ complexes are particularly interesting. These characteristics have not previously been reported for five-co-ordinate complexes, and a test of the generality of these trends must await the conclusion of studies on other systems.[23]

EXPERIMENTAL

The $[M(tda)ClO_4][ClO_4]$ complexes [tda = tris(2-dimethylaminoethyl)amine] were prepared as in the literature.[4] All solutions were prepared in triply distilled water and the perchloric acid and sodium perchlorate employed were AnalaR materials.

Kinetic measurements were made with a previously described stopped-flow spectrophotometer [24] of 1·96 mm optical path length and thermostatting control to at least ±0·05 K. In each kinetic run equal volumes (0·4 cm^3) of metal complex and acid solution (each of 2·0M ionic strength adjusted with sodium perchlorate) were mixed in the stopped-flow apparatus. No mixing effects were observed in blank runs. Each kinetic determination was made over six half-lives and in all cases only one relaxation was observed. Relaxation times were determined from oscilloscope traces, which were of excellent first-order character, using an exponential generator as described in the literature.[25] The standard deviations of the derived first-order rate constants were never greater than 3%. Static spectrophotometric measurements were made using a Perkin-Elmer P.E. 402 spectrophotometer.

We thank Professor E. F. Caldin and Dr. B. H. Robinson for their advice and assistance, and the Universities of Adelaide, South Australia, and New Hampshire, U.S.A., for granting leave of absence to S. F. L. and C. D. H. respectively.

[4/808 *Received*, 22*nd April*, 1974]

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[22] A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, 18.

[23] D. Weatherburn and S. F. Lincoln, personal communication; preliminary investigations of the substitution of the aqua-ligand in $[M(tda)H_2O]^{2+}$ by unidentate anions in aqueous solution indicate that the order of increasing lability for M^{2+} is $Co^{2+} < Ni^{2+} < Cu^+$.

[24] E. F. Caldin, J. E. Crooks, and A. Queen, *J. Phys.* (*E*), 1973, **6**, 930.

[25] J. E. Crooks, M. S. Zetter, and P. A. Tregloan, *J. Phys.* (*E*), 1970, **3**, 73.