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Synthesis, characterization and dissociation of mixed valent binuclear complexes

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Abstract—Two mixed metal binuclear complexes, $[(NH_3)_5Co^{III}(nta)Cu^{II}]^{2+}$ (**1**) and $[(NH_3)_5Co^{III}(pyc)Cu^{II}]^{4+}$ (**2**; nta = nitrilotriacetate and pyc = pyridine-2-carboxylate) have been synthesized and characterized on the basis of elemental analysis; UV–vis, IR, ESR spectroscopy; magnetic and electrochemical measurements. A stopped flow kinetic study indicated that the dissociation of $(NH_3)_5Co(nta)Cu^{2+}$ occured *via* spontaneous and acid catalysed paths. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: binuclear complex; dissociation; mixed valency; cobalt(III) complex; copper(II) complex; electrochemistry.

Mixed metal complexes have received considerable attention because of their importance in studies of magnetic and electronic coupling [1], development of methodology for synthesis of heterobimetallic catalytic precursors [2–4], *etc*. Although complexes of the type $[MM'L]^{n+}$ (M, M′ = same or different divalent metal ions, L = binucleating Schiff's base ligands) have been reported [1, 3, 5], mixed metal complexes of this class containing a trivalent and a bivalent metal ion are sparsely studied [1,6]. Also, in order to account for the metal ion catalysed aquation of certain carboxylato/aminoacidato(amine)cobalt(III), the formation of short-lived caroxylato/aminoacidato-bridged binuclear complexes involving the cobalt(III) substrates and the catalysed metal ions has been postulated [7–10]. Indirect evidence in favour of the formation of binuclear complexes *in situ* have been obtained from kinetic and equilibrium studies [11–13]. However, to our knowledge the isolation of such species in the solid state has so far been reported only in one case [14]. As such it was thought worthwhile to isolate and characterize some of the binuclear intermediates in the solid state. In this paper the synthesis of two mixed valent binuclear complexes, their characterisation by various physical methods and their acid catalysed dissociation are reported.

EXPERIMENTAL

Preparation of complexes

The cobalt(III) complexes, $[(NH_3)_5Co(pycH)](ClO_4)_3$ and $[(NH_3)_5Co(ntaH_2)](ClO_4)_2$ [pyc = pyridine-2-carboxylate ion and nta = $N(CH_2COO)_3^{3-}$] were prepared by the methods described earlier [9,10]. The mixed valent binuclear complexes were prepared as follows.

To an aqueous solution of the cobalt(III) complex, slightly more than 1 equiv amount of $Cu(ClO_4)_2$ solution was added and the pH of the solution was adjusted to *ca* 4.0 by addition of dilute NaOH. Addition of a few crystal of $NaClO_4$ followed by cooling to 10°C resulted in separation of pale blue crystals in the case of $(NH_3)_5Co(pycH)^{3+}$. In the case of $(NH_3)_5Co(ntaH_2)^{2+}$ the mixed solution was allowed to evaporate slowly at room temperature to obtain the desired product as blue–violet crystals. The crude products were recrystallized from hot water, filtered and washed with ice cold water, ethanol and finally with diethylether. The recrystallized products were air dried.

Physical measurements

Microanalyses were carried out on a C, H, N analyser at CDRI, Lucknow. Cobalt and copper were

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estimated by AAS using air–acetylene flame. The outer sphere perchlorate ions were estimated after separating the complex ion by passing the solution through a cation exchange resin column. The molar conductance of aqueous solutions were measured on a Systronics 304 digital conductivity meter. Electrochemical measurements of complexes in aqueous KCl medium were performed on a PAR cyclic voltameter (model 362) using a Pt working electrode. The potentials were measured against saturated calomel electrode (SCE). All other experimental details are same as described earlier [15].

Kinetic measurements

The kinetics of acid catalysed dissociation of $[(NH_3)_5Co(nta)Cu](ClO_4)_2$ were studied under pseudo-first-order conditions at $10.0 \leqslant T(^\circ C) \leqslant 30.0$, $0.011 \leqslant [H^+]$, mol dm$^{-3} \leqslant 0.275$ with [complex] $= 1.0 \times 10^{-3}$ and $I = 0.3$ mol dm^{-3}. The rate measurements were made at 280 nm using a fully automated Hi-Tech SF-51 (UK) stopped flow spectrophotometer. The pseudo-first-order rate constant for any run was taken to be the average from seven determinations and the error quoted is the standard deviation. All other kinetic details have been described in our earlier work [11]. The acid catalysed dissociation of $[(NH_3)_5Co(pyc)Cu](ClO_4)_4$ was, however, not possible as the rate of this reaction is faster than the mixing time of the stopped flow instrument.

RESULTS AND DISCUSSION

Characterization of complexes

The analytical data (see Table 1) and the molar ratio of Co : Cu : ClO_4 agreed well with the proposed molecular formulae. The values of molar conductance in aqueous solution for binuclear complexes **1** and **2** are comparable with the values expected for uni-bi- and uni-tetravalent electrolytes, respectively. UV–vis spectra of both the complexes are presented in Fig. 1. The absorption maxima ($^1T_{2g} \leftarrow {}^1A_{1g}$) at ~350 nm observed in the case of the parent Co^{III} complexes had either disappeared or was reduced to a shoulder in the binuclear complexes. The broad absorption peak between 715 and 760 nm was characteristic of the Cu^{II} ion [16] in these complexes. The absorption spectra of $Cu(OH_2)_6{}^{2+}$ usually consists of a broad band at ~830 nm ($^2T_{2g} \leftarrow {}^2E_g$). Therefore, this shift of absorption band towards lower wavelength in comparison to $Cu(OH_2)_6{}^{2+}$ is an indication of *N*-coordination, which produces a stronger ligand field on the Cu^{II} ion in the binuclear complex. However, no significant shift in the peak position at ~500 nm ($^1T_{1g} \leftarrow {}^1A_{1g}$) was observed in the binuclear complexes from that of the parent Co^{III} complexes although there was a slight increase in the extinction coefficient. This indicates that the gross symmetry of Co^{III} in the binuclear complexes remained unaffected.

The IR spectrum of the binuclear complexes displayed appreciable shifts in the position of some of the bands compared with those in the corresponding cobalt(III) complexes, especially in the region 1800–1400 cm^{-1}. The bands at 1732 and 1632 cm^{-1}, corresponding to the free carboxyl and coordinated carboxylate groups, respectively, in the $[(NH_3)_5Co(ntaH_2)](ClO_4)_2$, had either disappeared or week shifted to lower frequency (1600 cm^{-1}), respectively, in $[(NH_3)_5Co(nta)Cu](ClO_4)_2$, indicating that the free carboxyl groups are being coordinated in the binuclear complex. A new broad band appeared at 1578 cm^{-1} in the case of **1**, which was not observed in cobalt(III), which may attributed to carboxyl groups coordinated to copper(II) [17]. Similar shifts with the characteristic bands of coordinated carboxylate and C—N (ring) in $(NH_3)_5Co(pycH)^{3+}$ were observed due to bridging by carboxylate and C—N in **2**.

The X-band EPR spectra of the solid samples recorded at room temperature (303 K) displayed broad signals (see Fig. 2) with $g_{av} = 2.13$ and 2.06 for binuclear complexes **1** and **2**, respectively. The magnetic moments (μ_{eff}) at room temperature for the binuclear complexes **1** and **2**, after due diamagnetic

Table 1. Analytical, spectral, molar conductance and magnetic moments for the binuclear complexes[a]

	Elements (%)							
Complex	C	H	N	Cu	Co	λ_{max} (ε, dm^3 mol^{-1} cm^{-1})	Λ_m (ohm^{-1} cm^2)	μ_{eff} (B.M.)
$[RCo(pycH)](ClO_4)_3$	—	—	—	—	10.4	350(61.0)	—	—
					(10.4)	505(75.0)		
$[RCo(pyc)Cu](ClO_4)_4 \cdot 4H_2O$	9.3	3.6	10.7	8.0	7.6	507(82.9)	480	1.78
	(9.1)	(3.4)	(10.6)	(7.9)	(7.4)	715(33.1)		
$[RCo(ntaH_2)](ClO_4)_2$	14.1	4.3	16.5	—	11.2	350(56.6)	—	—
	(13.5)	(4.3)	(15.8)	—	(11.1)	500(69.3)		
$[RCo(nta)Cu](ClO_4)_3 \cdot 3H_2O$	11.2	4.3	13.1	9.8	9.0	502(79.3)	253	1.75
	(11.1)	(4.2)	(13.0)	(9.8)	(9.1)	762(57.0)		

[a] $R = (NH_3)_5$; $pycH = O_2CC_5H_4NH^+$; $ntaH_2 = (O_2CCH_2)_2N^+H_2(O_2CCH_2)$.

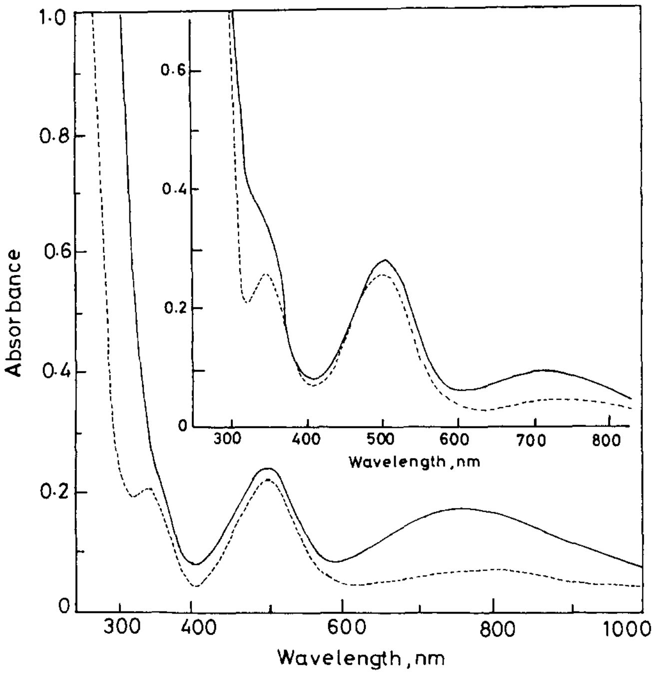

Fig. 1. UV–vis spectrum of $(NH_3)_5Co(nta)Cu^{2+}$ and $(NH_3)_5Co(pyc)Cu^{4+}$ (insert) in the presence (dotted lines) and absence (solid lines) of $HClO_4$. [complex] = 3.02×10^{-3} and 3.017×10^{-3} mol dm^{-3} for $(NH_3)_5Co(nta)Cu^{2+}$ and $(NH_3)_5Co(pyc)Cu^{4+}$, respectively.

correction for ligands and counter ions using Pascals's constants [18], were found to be 1.75 and 1.78 B.M. per mole of Cu atom, respectively. These are comparable with the values expected for one Cu^{II} ion, indicating the absence of any magnetic interaction between Cu^{II} ions of different molecules.

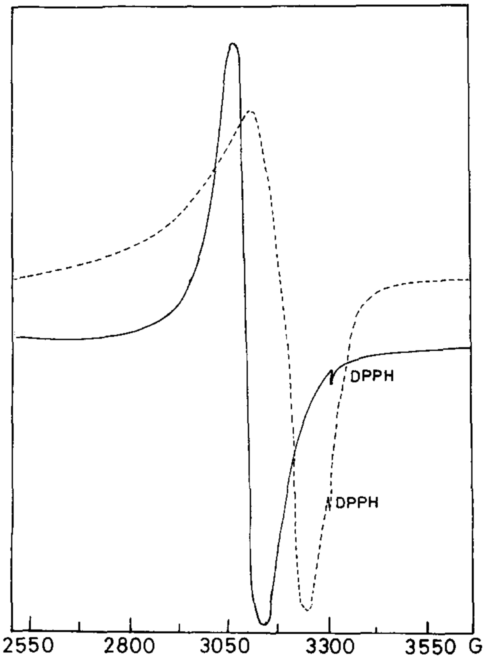

Fig. 2. X-band ESR spectrum of $(NH_3)_5Co(nta)Cu^{2+}$ (solid line) and $(NH_3)_5Co(pyc)Cu^{4+}$ (dotted lines).

The cyclic voltammograms of both the binuclear complexes along with those of $Cu(ClO_4)_2$ and a 1 : 1 mixture of $Cu(ClO_4)_2$ and nta are illustrated in Fig. 3. In cathodic sweep the waves occurred at 0.16, −0.26 and −0.42 V for complex **1** are attributed to the reduction Cu^{II}–Cu^{I}, Cu^{I}–Cu^{0} and Co^{III}–Co^{II}, respectively. In contrast, only two waves at −0.23 and −0.4 V are, however, observed for complex **2**. The more positive redox potentials for the step Cu^{II}–Cu^{I} compared to same with Co^{III}–Cu^{II} dinuclear Cu^{II} complexes or copper acetate [1,19,20] indicate that reduction of Cu^{II} in these binuclear complexes is more favourable than in the latter cases. Oxidation in both the complexes occurred in a non-reversible manner.

Kinetics

The binuclear complexes in aqueous solution ($3.0 \leq pH \leq 8.0$) are stable for a long period. However, at higher acid concentrations they underwent dissociation leading to the parent Co^{III} complexes and Cu^{II} (see Fig. 1). The rate data for the acid-catalysed dissociation of $[(NH_3)_5Co(nta)Cu]^{2+}$ at various temperatures are collected in Table 2. The plots of k_{obs} *vs* $[H^+]$ are linear with small positive intercepts on the rate axis, indicating that acid-cat-

Table 2. Rate and activation parameters for the acid catalysed dissociation of $(NH_3)_5Co(nta)Cu^{2+}$; [complex] = 1.0×10^{-3}, $I = 0.3$ mol dm^{-3}; $\lambda = 280$ nm

	10.0 ± 0.1	15.0 ± 0.1	20.0 ± 0.1	25.0 ± 0.1	30.0 ± 0.1 °C
10^2 [H^+], mol dm^{-3}			k_{obs} (s^{-1})		
1.10	4.8 ± 0.1	6.1 ± 0.1	8.8 ± 0.2	11.1 ± 0.2	15.0 ± 0.2
2.75	11.2 ± 0.3	16.1 ± 0.2	19 ± 1	24 ± 1	31 ± 1
5.50	22.8 ± 0.4	30.0 ± 0.2	39 ± 2	46 ± 1	57 ± 1
8.80	38.0 ± 0.4	49 ± 1	60 ± 2	71 ± 4	95 ± 3
11.0	48 ± 1	61 ± 2	74 ± 1	93 ± 4	107 ± 4
13.2	58 ± 2	69 ± 2	88 ± 3	104 ± 4	134 ± 5
16.5	70 ± 1	88 ± 2	110 ± 5	143 ± 8	176 ± 7
22.0	92 ± 3	120 ± 4	151 ± 5	180 ± 7	222 ± 9
27.5	117 ± 4	143 ± 6	182 ± 8	—	—
k_1 (s^{-1})	0.18 ± 0.035	0.45 ± 0.08	1.49 ± 0.16	2.39 ± 0.38	4.17 ± 0.33
k_2 (dm^3 mol^{-1} s^{-1})	428 ± 15	547 ± 15	662 ± 20	799 ± 19	981 ± 17
$\Delta H^{\pm}$ (kJ mol^{-1}) = 99 ± 11;[a] 27 ± 1[a] (18.5 ± 7.6)					
$\Delta S^{\pm}$ (J K^{-1} mol^{-1}) = 97 ± 36;[a] −99 ± 4[a] (−133 ± 25)					

[a] Obtained from the temperature dependence rate data for k_1 and k_2, respectively. The bracketed values are the same obtained from previous study [11].

alysed dissociation of $(NH_3)_5Co(nta)Cu^{2+}$ is the significant path under these conditions. Consistent with this observation, the rate expression is given by eq. (1).

$$k_{obs} = k_1 + k_2[H^+], \qquad (1)$$

where k_1 and k_2 are the spontaneous and acid-catalysed dissociation rate constants, respectively. The values of k_1 and k_2 obtained from the least-squares fitting of k_{obs} and $[H^+]$ data and their associated activation parameters are also collected in Table 2. The spontaneous dissociation rate constants (k_1) are small, but relatively higher than the same for $Cu(nta)^-$ ($k_1 \simeq 2 \times 10^{-5}$ s^{-1}, 25°C).* On the other hand, $[(NH_3)_5Co(nta)Cu]^{2+}$ is kinetically $\sim 10^7$ times more stable than (monoacetato)copper(II) ($k_1 = 1.93 \times 10^7$ s^{-1}, 25°C).* This indicates that Cu^{2+} in the binuclear complex is not bound to nta in an unidentate fashion (as in the case of copper acetate) rather all unbound donor sites of nta are being coordinated to form the chelate structure. The crystal structure and NMR studies [23–25] of $[Al(nta)(OH_2)_2]\cdot(CH_3)_2CO\cdot H_2O$ and $Na[Cu(nta)(OH_2)_2]\cdot H_2O$ also provide further evidence for the chelate structure where all donor groups of nta are coordinated to Cu^{II}.

The rate constant for the acid catalysed path (k_2 path) are, however, 2–3 times higher than those obtained from the dissociation of $[(NH_3)_5Co(nta)Cu]^{2+}$ (e.g. $k_2 = 320 \pm 30$ dm^3 mol^{-1}s^{-1}, 20°C)

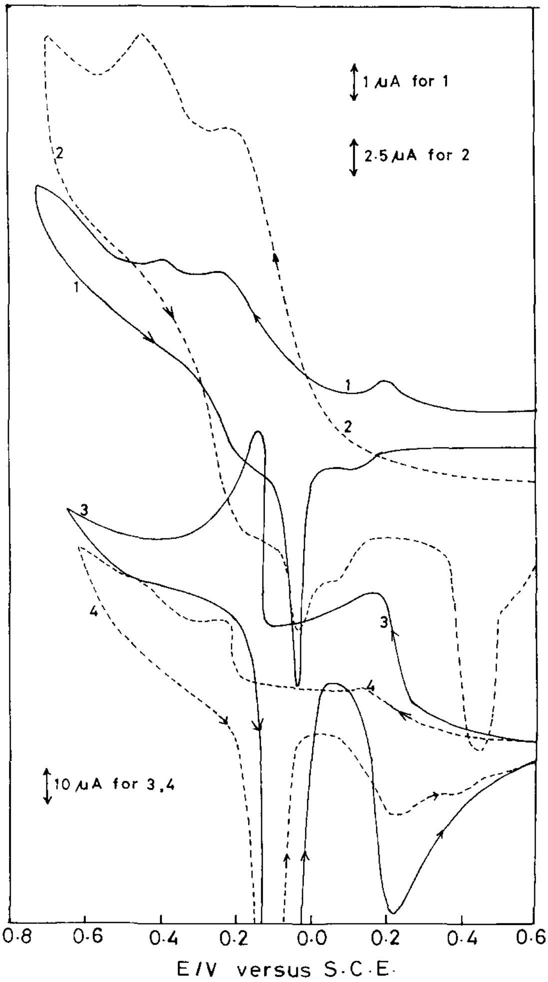

Fig. 3. Cyclic voltammogram of $(NH_3)_5Co(nta)Cu^{2+}$ (**1**) $(NH_3)_5Co(pyc)Cu^{4+}$ (**2**), $Cu(ClO_4)_2$ (**3**) and 1 : 1 mixture of $Cu(ClO_4)_2$ and nta (**4**) in aqueous KCl medium at scan rate of 50 mV s^{-1}.

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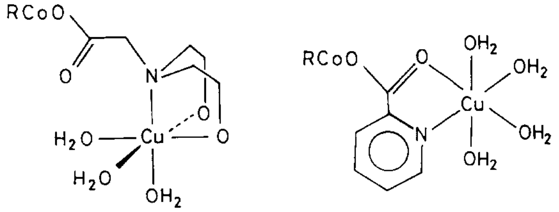
*The tentative values of spontaneous dissociation rate constants (k_1) for $Cu(nta)^-$ and $Cu(OAc)^+$ are calculated from the values of stability constants of $Cu(nta)^-$ ($K_M = 1 \times 10^{13}$ dm^3 mol^{-1}, 25°C), $Cu(OAC)^+$ ($K_M = 77.6$ dm^3 mol^{-1}, 25°C) [21] and forward rate constants ($k_f^{nta} = 2.0 \times 10^8$ dm^3 mol^{-1} s^{-1}, $k_f^{OAC} = 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}; 25°C) [22] using the relationship $K_M = k_f/k_1$.



(1) (2)

R = $(NH_3)_5$

Possible structures of $[(NH_3)_5Co(nta)Cu]$ $(ClO_4)_2 \cdot 3H_2O$ and $[(NH_3)_5Co(pyc)Cu]$ $(ClO_4)_4 \cdot 4H_2O$.

[11] which is prepared *in situ* by adding excess Cu^{II} (at least 10 times) to $[(NH_3)_5Co(ntaH_2)]^{2+}$. The discrepancy between these values can be attributed to the fact that the formation of $[(NH_3)_5Co(nta)Cu]^{2+}$ is also predominating (especially at low acid concentration) in the latter case, which led to low values of dissociation rate constants. The activation parameters for the k_2 path are comparable in both cases. The H^+-promoted Cu—N bond cleavage being the most likely rate determining step [26–28].

As the dissociation of $[(NH_3)_5Co(pyc)Cu]^{4+}$ is faster than the mixing time of stopped flow, the kinetic evidence in favour of the chelated stucture is provided by comparing the dissociation rate constant of its Co^{II} analogue [29]. The spontaneous dissociation rate constant of $[(NH_3)_5Co(pyc)Co]^{4+}$ (19.3 ± 0.3 s^{-1}, 20°C) [29] compares well with the same for mono(pyridine-2-carboxylato)cobalt(II) (20 s^{-1}, 20°C) [30]. This is contrary to the expectation that Co^{II} is bound to pyridine-2-carboxylate through pyridine-N in a unidentate fashion; a chelate ring involving pyridine-N and the unbound carboxylate end of the half bound carboxylate group is more likely (see structure).

On the basis of the above physicochemical studies and evidence from earlier studies [9–11,23–25,29], the tentative structure of the binuclear complexes can be assigned, as given in structures **I** and **II**.

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