Contrast in the Effect of Penta-amminecobalt(III) on the Chemical Properties of Nicotineamide and Isonicotineamide Ligands

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The specific rates of reaction of hydroxyl radicals with L, HL^+, and $[Co(NH_3)_5L]^{3+}$ [L = pyridine (py), nicotineamide (na), and isonicotineamide (ina)] have been measured. The order $k(OH + L) > k\{OH + [Co(NH_3)_5L]^{3+}\} > k(OH + HL^+)$ occurs with the exception $k\{OH + [Co(NH_3)_5(na)]^{3+}\} > k(OH + na)$. The spectra of the intermediates $L{\cdot}OH$ and $[Co^{III}(NH_3)_5(L{\cdot}OH)]$ formed in these reactions have been measured. The spectra of $L{\cdot}OH$ are similar to those of $[Co^{III}(NH_3)_5(L{\cdot}OH)]$ for L = py and ina. However, $\lambda_{max.}$ = 385 nm for the intermediate formed in the reaction $OH + [Co(NH_3)_5(na)]^{3+}$ whereas $\lambda_{max.}$ = 315 nm for $na{\cdot}OH$. Furthermore the radical $[(NCS)]_2^-$ reacts with $[Co(NH_3)_5(na)]^{3+}$ with $k = 3.3 \times 10^8$ dm^3 mol^{-1} s^{-1} although it does not react with na and with py, ina, and their complexes. These results are discussed.

REDUCTION of complexes of the type $[Co^{III}(NH_3)_5L]$ (L = a pyridine derivative) by some reducing agents was found to be autocatalytic for some pyridine derivatives with α or γ substituents.[1] No autocatalytic reductions were observed for the corresponding ligands with β substituents.[1] Thus the reduction of $[Co(NH_3)_5(ina)]^{3+}$ (ina = isonicotineamide, $NC_5H_5CONH_2$-4) by Eu^{2+}(aq) is autocatalytic, whereas the reduction of $[Co(NH_3)_5(na)]^{3+}$ (na = nicotineamide, $NC_5H_5CONH_2$-3) is not autocatalytic.[1c] Recently we suggested[2] that these results stem from the fact that Co^{III} affects the specific rate of reduction of the ligand by decreasing it for ina and increasing it for na relative to $Hina^+$ and Hna^+ respectively.

Hydroxyl radicals are known to add to aromatic rings in an electrophilic process.[3] It seemed of interest to study the effect of co-ordination of pyridine (py), na, and ina to $[Co^{III}(NH_3)_5]$ on the reactivity towards hydroxyl radicals. The results might help in elucidating the effect of ligation of the pyridine derivatives to the central cobalt(III) atom on the electron density on the aromatic ring.

EXPERIMENTAL

Materials.—All the solutions were prepared from triple distilled water. The complexes $[Co(NH_3)_5(py)][ClO_4]_3$, $[Co(NH_3)_5(na)][ClO_4]_3$, and $[Co(NH_3)_5(ina)][ClO_4)]_3$ were prepared according to procedures given in the literature.[4] Their purity was checked by comparing their spectra with those reported in the literature.[4] Both $\lambda_{max.}$ and $\varepsilon_{max.}$ were within ±2 nm (±5%) of those reported in the literature.[4] Dinitrogen mono-oxide and argon were purified from trace amounts of oxygen by bubbling through three wash bottles containing acidic solutions (H_2SO_4) of $V[SO_4]$ followed by two wash bottles containing $Na[OH]$ solution and triple distilled water respectively. All the other reagents were of AnalaR grade and were used without further purification.

Procedure.—The procedure of preparation of the samples for the pulse-radiolysis experiments was identical with that described earlier in detail.[5] The pulse-radiolysis experiments were carried out using 0.05—0.5-μs, 5-MeV, 200-mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was 100—1 500 rad.† The experimental set-up in Jerusalem and the method used for evaluating the results have been described elsewhere in detail.[6] All the experiments were at room temperature, 22 ± 2 °C. Low-dose-rate irradiations were carried out in a Noratom ^{60}Co γ source with a dose rate of 1.8×10^4 rad min^{-1}. The yield of Co^{2+}(aq) was determined by the method of Katakis and Allen.[7]

RESULTS

Dinitrogen mono-oxide saturated solutions (*ca.* 2×10^{-2} mol dm^{-3}) at pH 5.9 ± 0.2 which contained L and $[Co^{III}(NH_3)_5L]$ (L = py, na, and ina) in the concentration range 1×10^{-4}—20×10^{-4} mol dm^{-3}, or argon-saturated solutions

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† 1 rad = 10^{-2} J kg^{-1}, 1 eV ≈ 1.6×10^{-19} J.

[1] (*a*) J. R. Barker, jun., and E. S. Gould, *J. Amer. Chem. Soc.*, 1971, **93**, 4045; (*b*) E. D. Dockal and E. S. Gould, *ibid.*, 1972, **94**, 6673; (*c*) C. Norris and F. Nordmeyer, *ibid.*, 1971, **93**, 4044; (*d*) H. C. Chen and E. S. Gould, *ibid.*, 1973, **95**, 5539.

[2] H. Cohen and D. Meyerstein, *Israel J. Chem.*, 1974, **12**, 1049.

[3] M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.*, 1966, **70**, 2660; P. Neta and L. M. Dorfman, *Adv. Chem. Ser.*, 1968, **81**, 222.

[4] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1162.

[5] D. Meyerstein and W. A. Mulac, *Inorg. Chem.*, 1970, **9**, 1762; H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4179; *Inorg. Chem.*, 1974, **13**, 2434.

[6] Internal Report of the Linac. Lab., The Hebrew University of Jerusalem, Jerusalem.

[7] D. Katakis and A. O. Allen, *J. Phys. Chem.*, 1964, **68**, 1359.

at pH 1 which contained L in the concentration range 5×10^{-3}—20×10^{-3}, were irradiated. The formation of intermediates, which absorb light in the near u.v. region, was observed. The kinetics of formation of the intermediates obeyed a pseudo-first-order rate law in the concentration of L, $[Co^{III}(NH_3)_5L]$, or HL^+ respectively.* The specific rates of reactions measured are summarized in Table 1. The specific rates of the reactions OH + L and OH + $[Co^{III}(NH_3)_5L]^{3+}$ were also measured by competition with $[NCS]^-$.[8] The results are in full agreement with those in Table 1. The spectra of the intermediates are plotted in Figure 1. The intermediates L·OH (formed in the reaction with L) disappear in second-order reactions with the specific rates $2k = 1.2 \times 10^9$, 2.0×10^9, and 2.3×10^9 $dm^3\ mol^{-1}\ s^{-1}$ for L = py, na, and ina respectively.

The intermediate formed by the reaction OH + $[Co(NH_3)_5(py)]^{3+}$ disappears in three time-separated processes: (*a*) a second-order reaction with $2k = 1.3 \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$; (*b*) a first-order process with $k_{obs.}{}^b = (4 \pm 2) \times 10^1\ s^{-1}$; (*c*) a third process which also fits a first-order rate law with $k_{obs.}{}^c = 0.3 \pm 0.1\ s^{-1}$. The rates of the latter two processes were independent of dose and complex concentration.† The intermediates formed from the reactions with $[Co(NH_3)_5(na)]^{3+}$ and $[Co(NH_3)_5(ina)]^{3+}$ disappeared in second-order reactions with $2k = 3.0 \times 10^9$ and 6.0×10^9 $dm^3\ mol^{-1}\ s^{-1}$ respectively. The final products had only a weak absorption at $\lambda \geqslant 320$ nm. The yield of $Co^{2+}(aq)$ as a final product was measured. The results are summarized in Table 2.

TABLE 1

Specific rates of reaction of hydroxyl radicals with L, HL^+, and $[Co^{III}(NH_3)_5L]$ [a]

	$k/dm^3\ mol^{-1}\ s^{-1}$		
	OH + L	OH + HL^+	OH + $[Co^{III}(NH_3)_5L]$
Pyridine	4.5×10^9	3.4×10^7 [b]	4.2×10^8
Nicotineamide	1.4×10^9	1.8×10^8	2.1×10^9
Isonicotineamide	1.6×10^9	8.0×10^7	8.0×10^8

[a] Accuracy ±15%. [b] Value taken from ref. 9.

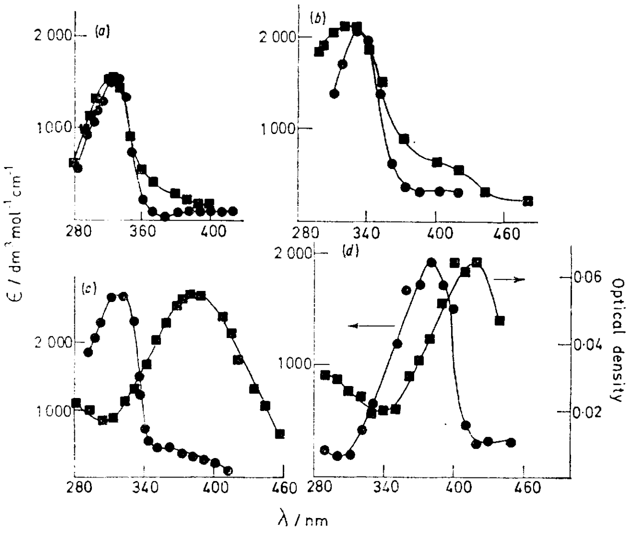

FIGURE 1 Spectra of the intermediates formed in the reaction of L and $[Co^{III}(NH_3)_5]$ (L = py, na, and ina) with hydroxyl radicals and of $[Co(NH_3)_5(na)]^{3+}$ with $[(NCS)_2]^-$ radicals: (a) py·OH (●), $[Co^{III}(NH_3)_5(py{\cdot}OH)]$ (■); (*b*) ina·OH (●), $[Co^{III}(NH_3)_5(ina{\cdot}OH)]$ (■); (*c*) na·OH (●), intermediate formed in the reaction OH + $[Co^{III}(NH_3)_5(na)]$ (■); (*d*) intermediate formed by the reaction OH + $[Co^{III}(NH_3)_5(na)]$ (●), intermediate formed by the reaction $[(NCS)_2]^-$ + $[Co^{III}(NH_3)_5(na)]$ (■)

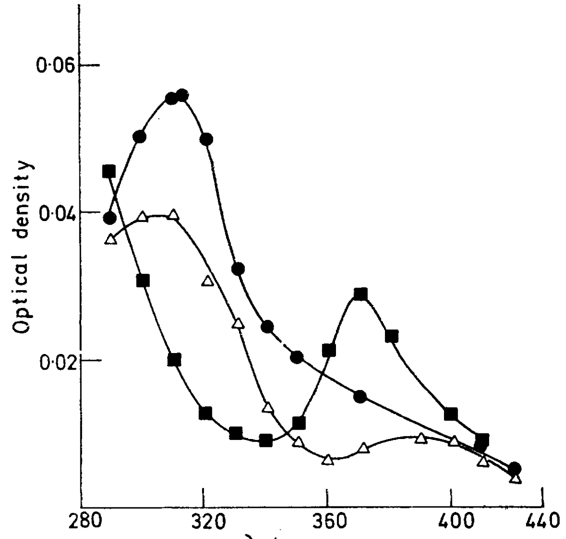

FIGURE 2 Spectra of the intermediates formed by the reaction of OH with $[Co^{III}(NH_3)_5(py)]$ measured 10 μs (●), 1 ms (■), and 50 ms (△) from the end of the pulse

TABLE 2

Yields of $Co^{2+}(aq)$ [a]

	$G[Co^{2+}(aq)]$	
Complex	*b*	*c*
$[Co(NH_3)_5(py)]^{3+}$	1.0	3.2
$[Co(NH_3)_5(na)]^{3+}$	2.0	3.6
$[Co(NH_3)_5(ina)]^{3+}$	1.5	3.0

[a] N_2O-saturated solutions containing 1×10^{-4}—3×10^{-4} mol dm^{-3} complex were irradiated by ⩽3 000 rad. Accuracy in the determinations of $Co^{2+}(aq)$ $G \pm 0.4$. [b] Irradiated at the Linac. [c] Irradiated at the ^{60}Co γ source.

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* The possibility that the reactions of hydrogen atoms contribute to the rate of reaction between OH and HL^+ at pH 1.0 was ruled out by blank experiments in which 0.10 mol dm^{-3} Me_3COH was added to the solutions.

† M. Z. Hoffman and D. W. Kimmel (*J.C.S. Chem. Comm.*, 1975, 549) studied the reaction OH + $[Co(NH_3)_5(py)]^{3+}$. Their specific rate for this reaction is 50% higher than that reported here. We believe that the difference is due to the use of larger pulses which cause a contribution from the OH + OH $\longrightarrow$ H_2O_2 reaction. The values of $\lambda_{max.}$ and $\varepsilon_{max.}$ for $[Co(NH_3)_5(py{\cdot}OH)]^{3+}$ are in agreement with our findings. Also the yield of $Co^{2+}(aq)$ at low dose rate is in fair agreement with our results. However, these workers do not report the yield of $Co^{2+}(aq)$ in pulse experiments which differs considerably. Furthermore they observed only one intermediate which disappeared with a rate of 6.0 s^{-1} whereas we observed three successive intermediates (Figure 2). We have no explanation for these discrepancies. We have checked our results with three samples of complex synthesized independently. We have also checked the effect of added O_2 which resulted in the formation of stable products absorbing above 320 nm. However, we were unable to reproduce the results of Hoffman and Kimmel. This disagreement in the experimental results is not directly related to the main subject of the present study.

[8] M. S. Matheson and L. M. Dorfman, ' Pulse Radiolysis,' M.I.T. Press, Cambridge, Massachusetts, 1969, chs. 6 and 7.

Solutions saturated with N_2O at pH 5.9 ± 0.2 and containing $[NH_4][NCS]$ in the concentration range 7×10^{-5}—8×10^{-3} mol dm^{-3} and different concentrations of $[Co(NH_3)_5(na)]^{3+}$ were irradiated. The formation of $[(NCS)_2]^-$ was observed. The $[(NCS)_2]^-$ radicals disappeared in the presence of $[Co(NH_3)_5(na)]^{3+}$ in a pseudo-first-order reaction in the complex concentration with $k = 3.3 \times 10^8$ dm^3 mol^{-1} s^{-1}. The disappearance of the $[(NCS)_2]^-$ was followed by the formation of a strong absorption in the near u.v. The spectrum of the intermediate formed is given in Figure 1(*d*). The latter absorption band disappeared in a second-order reaction with $2k/\varepsilon = (7 \pm 1) \times 10^5$ cm s^{-1}. No reaction of $[(NCS)_2]^-$ with free na, ina, py, and with the complexes $[Co(NH_3)_5(py)]^{3+}$ and $[Co(NH_3)_5(ina)]^{3+}$ was observed.

DISCUSSION

The radiolysis of water may be described [8] by equation (1), the yield of the products in neutral solutions being

$$H_2O \xrightarrow{\gamma e^-} e^-(aq),\ H,\ OH,\ H_2,\ H_2O_2,\ [H_3O]^+ \quad (1)$$

$G[e^-(aq)] = 2.65$, $G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2O_2) = 0.75$, and $G(H_2) = 0.45$ (where G is defined as the number of molecules of product formed on absorption of 100 eV by the sample). Reactions (2)—(5)

$$e^-(aq) + N_2O + H_2O \longrightarrow N_2 + OH^- + OH,$$
$$k_2 = 5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 9)} \quad (2)$$

$$e^-(aq) + L \xrightarrow{H^+} HL\cdot,$$
$$k_{3a} = 1 \times 10^{10}\text{—}4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 10)} \quad (3a)$$

or

$$e^-(aq) + [Co^{III}(NH_3)_5L] \longrightarrow Co^{2+}(aq) + 5NH_3 + L,$$
$$k_{3b} = 6 \times 10^{10}\text{—}10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 9)} \quad (3b)$$

$$H + L \longrightarrow \text{products} \quad (4a)$$

or $$H + [Co^{III}(NH_3)_5L] \longrightarrow \text{products} \quad (4b)$$

$$OH + L \longrightarrow \text{products} \quad (5a)$$

or $$OH + [Co^{III}(NH_3)_5L] \longrightarrow \text{products} \quad (5b)$$

might occur when N_2O-saturated neutral solutions containing 5×10^{-5}—2×10^{-3} mol dm^{-3} L or $[Co^{III}(NH_3)_5L]$ are irradiated. Under our experimental conditions, $[Co(NH_3)_5L]^{3+} \leqslant 5 \times 10^{-4}$ mol dm^{-3}, most of the hydrated electrons reacted *via* reaction (2) to yield OH radicals. Furthermore, the products of reaction (3b) do not absorb light in the region studied. No appreciable absorption was observed in N_2O-saturated neutral solutions containing 1.0 mol dm^{-3} Bu^tOH and L or $[Co(NH_3)_5L]^{3+}$. Under these conditions all OH radicals react *via* (6) and the radicals $\cdot CH_2CMe_2OH$ do

$$OH + Bu^tOH \longrightarrow \cdot CH_2CMe_2OH + H_2O,$$
$$k_6 = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 9)} \quad (6)$$

not absorb in the region studied. These experiments indicate that the absorption formed by the reactions of hydrogen atoms [reaction (4)] can be neglected under our experimental conditions. Therefore we conclude that the intermediates observed [Figure 1(*a*)—(*c*)] are the products of reaction of hydroxyl radicals with the solutes [reaction (5)].

Spectra of the Intermediates.—The spectroscopic results [Figure 1(*a*)—(*c*)] indicate that the intermediates formed in the reactions $OH + [Co(NH_3)_5L]^{3+}$ (L = py and ina) are of similar nature to those formed in the reactions $L + OH \longrightarrow L\cdot OH$. Thus $\lambda_{max.}$ and $\varepsilon_{max.}$ are unaffected, within the experimental accuracy, on ligation to $[Co(NH_3)_5]^{3+}$. The absorption bands in the complexed intermediates are however somewhat broader and have a slightly different shape. We therefore conclude that hydroxyl radical adds to the pyridine ring in the complex in a similar fashion to the reaction with the free ligands.

On the other hand $\lambda_{max.}$ of the absorption spectrum of the intermediate formed in the reaction $OH + [Co(NH_3)_5(na)]^{3+} \longrightarrow$ Intermediate 1 is shifted by *ca.* 70 nm to the red relative to that of na·OH [Figure 1(*c*)]. Thus the spectroscopic data suggest that the nature of the intermediate differs from those of $[Co(NH_3)_5(py\cdot OH)]$ and $[Co(NH_3)_5(ina\cdot OH)]$. This conclusion is corroborated by the kinetic results (see below).

Kinetics of the Reaction $OH + [Co^{III}(NH_3)_5L]$.—The results in Table 1 clearly demonstrate that $[Co(NH_3)_5]^{3+}$ affects the reactivity of na in a different manner to that of py and ina. Hydroxyl radicals are known to add to aromatic compounds by an electrophilic process.[3] Indeed for all pyridyl derivatives $k(OH + L) > k(OH + HL^+)$ (Table 1 and ref. 10). The observed order of reactivities $L > [Co(NH_3)_5L]^{3+} > HL^+$ for L = py and ina is in agreement with the expected relative effects of H^+ and $[Co(NH_3)_5]^{3+}$ as electron-withdrawing groups.

The order of reactivity of OH radicals for L = na, *i.e.* $[Co(NH_3)_5(na)]^{3+} > na > Hna^+$, can clearly not be explained by this argument. Furthermore it was found that $[(NCS)_2]^-$ which is a weaker oxidant reacts with $[Co(NH_3)_5(na)]^{3+}$ with $k = 3.3 \times 10^8$ dm^3 mol^{-1} s^{-1}, whereas it is unreactive towards the other two complexes and the three free ligands. The absorption spectrum of the intermediate formed in the latter reaction resembles that of intermediate 1, although it is not identical [Figure 1(*d*)].

Conclusions.—The kinetic and spectroscopic results clearly point out that the $[Co(NH_3)_5]^{3+}$ group affects the properties of na differently compared with py and ina as ligands. The results seem to suggest that the site of attack of the hydroxyl radical on na is changed on ligation. The increase in reactivity on ligation indicates that the attack is not on the aromatic ring thus suggesting attack on the amide group.

Finally it is of interest to point out that this peculiarity in the behaviour of $[Co(NH_3)_5(na)]^{3+}$ is not only for its oxidation by OH radicals but also for its reduction by $Eu^{2+}(aq)$ where $k\{Eu^{2+} + [Co(NH_3)_5(na)]^{3+}\} > k(Eu^{2+} + Hna^+)$ whereas $k(Eu^{2+} + Hina^+) > k\{Eu^{2+} +$

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[9] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

[10] M. Simic and M. Ebert, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 259; B. Cercek and M. Ebert, *Trans. Faraday Soc.*, 1967, **63**, 1687.

$[Co(NH_3)_5(ina)]^{3+}\}$.[1,2] These results clearly indicate that $[Co(NH_3)_5]^{3+}$ affects differently the chemical properties of nicotineamide and isonicotineamide. The difference is probably due to the different resonance structures for β- and γ-substituted pyridines.

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