Inorganica Chimica Acta, 154 (1988) 63–66

Redox Potentials of Trinuclear μ-Oxo Ruthenium Acetate Clusters with N-heterocyclic Ligands

HENRIQUE E. TOMA, CARLOS J. CUNHA and CECILIA CIPRIANO

Instituto de Quimica, Universidade de São Paulo, Caixa Postal 20780, São Paulo, SP, Brazil

(Received April 13, 1988)

Abstract

The trinuclear clusters of general composition $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3]$, where N-Het = pyridine and pyrazine derivatives, exhibit a series of reversible waves in the range of -1.8 to 2.4 V *versus* SHE, in acetonitrile, ascribed to the successive $[\text{cluster}]^{-2/-1/0/+1/+2/+3}$ redox couples. The redox potentials decrease with the pK_a of the N-heterocyclic ligands according to the equations $E°(+3/+2) = 2.24–0.023$ pK_a; $E°(+2/+1) = 1.34–0.029$ pK_a; $E°(+1/0) = 0.36–0.039$ pK_a and $E°(0/-1) = -0.68–0.074$ pK_a. The dependence is greater at lower oxidation states, reflecting the role of π-backbonding in the complexes.

Introduction

Ruthenium clusters of general formula $[Ru_3O(OOCCH_3)_6L_3]$ exhibit a triangular structure strongly held by acetate bridges and a central μ-oxo bridge [1–3], as well as by extended metal–metal bonds. These complexes are of great interest because of their extensive redox and mixed-valence chemistry [1–6]. In this work we describe the redox behaviour of a series of clusters with N-heterocyclic ligands, emphasizing the correlations with the basicity properties, at the several oxidation states.

Experimental

The $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3](PF_6)$ clusters, where N-Het = pyridine (py), 4-amino pyridine (ampy), 4-tert-butyl pyridine (tbpy), isonicotinamide (adpy), 4-acetyl pyridine (acpy), methyl isonicotinate (mspy), pyrazine (pz), 2-aminopyrazine (ampz) and 2,6 dimethyl pyrazine (dmpz) were synthesized according to the procedures reported for related complexes [4]. C, H, and N microanalyses (Table I) were consistent with the proposed compositions.

Cyclic voltamperometry was carried out with a Princeton Applied Research (PAR) instrument, consisting of a model 173 potentiostat and a model 175 universal programmer. A platinum disc electrode was employed for the measurements, using the conventional Luggin capillary arrangement with the $Ag/AgNO_3$ (0.010 mol dm^{-3}) reference electrode ($E° = 0.503$ V *versus* SHE [7]) in acetonitrile solution containing 0.100 mol dm^{-3} tetraethylammonium perchlorate (TEAP). A platinum wire was used as the auxiliary electrode. Acetonitrile, HPLC

TABLE I. Microanalytical and Spectroscopic Data for $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3](PF_6)$ Clusters[a]

N-Het	C (%)	H (%)	N (%)	λ_{max} (nm)[b]	(log ϵ)
py	30.6(30.7)	3.2(3.2)	3.7(3.9)	690(3.75)	340(sh)
tbpy	38.3(38.2)	4.7(4.8)	3.4(3.2)	693(3.83)	345(sh)
adpy[c]	30.1(31.9)	3.6(3.2)	7.6(7.5)	700(3.83)	345(4.02)
acpy[c]	34.9(35.2)	3.5(3.5)	3.8(3.7)	703(3.80)	370(3.98)
mspy[c]	33.5(33.8)	3.5(3.4)	3.4(3.6)	701(3.86)	365(4.07)
ampy[d]	27.6(28.0)	3.5(3.6)	6.4(7.2)	686(3.81)	381(3.99)
pz	26.5(27.2)	2.9(2.8)	7.8(7.9)	706(3.75)	358(3.99)
dmpz	31.0(31.5)	3.6(3.7)	7.0(7.3)	703(3.84)	345(4.08)
ampz	25.5(26.1)	3.2(3.0)	11.3(11.4)	700(3.72)	360(sh)

[a] Calculated values in parentheses. [b] Absorption spectra in acetonitrile solutions. [c] BF_4^- salts. [d] Calculated values including 3 molecules of H_2O.

0020-1693/88/$3.50

© Elsevier Sequoia/Printed in Switzerland

grade (Aldrich), was used as supplied. The electronic spectra of the complexes were recorded on a Hewlett-Packard model HP 8451-A diode-array spectrophotometer.

Results and Discussion

The $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3](PF_6)$ clusters were synthesized in the formal $Ru^{III}Ru^{III}Ru^{III}$ oxidation states. The complexes are stable and soluble in acetonitrile, yielding blue-greenish solutions. The visible electronic spectra (Fig. 1) consist of a broad absorption band around 700 nm, ascribed to metal–metal transitions in the trinuclear Ru_3O centre [4]. A second band is observed in the near-UV region, around 350 nm, arising from charge-transfer transitions associated with the Ru(III)–N-heterocyclic chromophore. The spectral data for the complexes are summarized in Table I.

The cyclic voltamperograms of the trinuclear clusters in acetonitrile solutions, exhibit a set of four or five redox waves in the range of potentials from −1.8 to 2.4 V *versus* SHE. Typical examples can be seen in Fig. 2. Except for the waves near the limiting potentials, the electrochemical behaviour was practically reversible [8], with the ratios of the anodic and cathodic peak currents very close to the unity. The separation between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials was approximately 60 mV, at low potential scan rates (e.g. 20 mV s^{-1}), increasing in some cases, up to 80 mV at 200 mV s^{-1}.

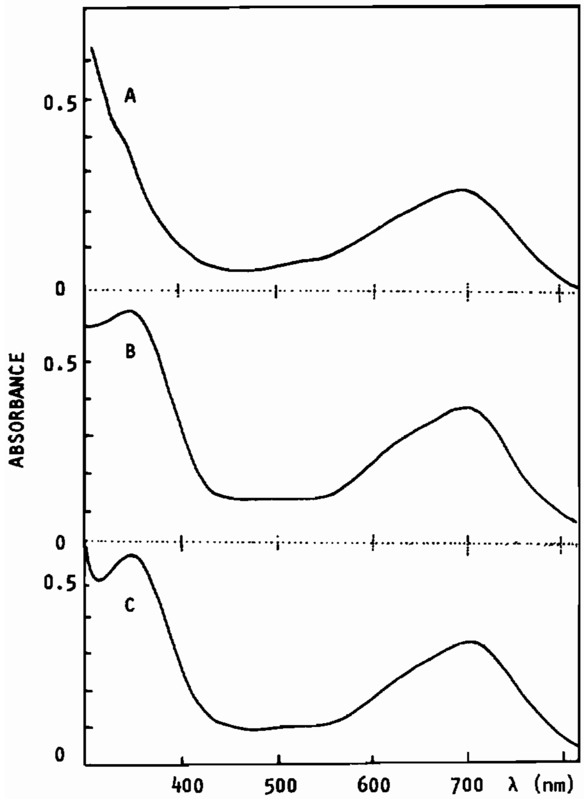

Fig. 1. Electronic spectra of $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3]$ clusters in acetonitrile solutions, N-Het = 4-tert-butylpyridine (A); isonicotinamide (B), and 2,6 dimethyl pyrazine (C).

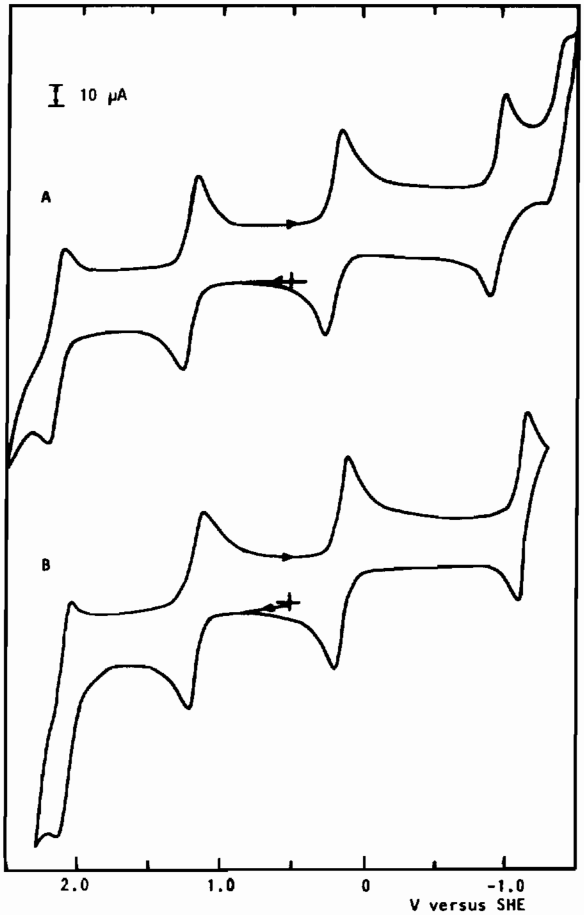

Fig. 2. Cyclic voltamperograms of $[Ru_3O(OOCCH_3)_6(N\text{-Het})_3]$ clusters (5×10^{-3} mol dm^{-3}) in acetonitrile solutions, scan rate = 100 mV s^{-1}, [TEAP] = 0.100 mol dm^{-3}, N-Het = isonicotinamide (A), or 4-tert-butylpyridine (B).

The redox potentials shown in Table II were calculated as $(E_{pa} + E_{pc})/2$, coinciding with the $E_{1/2}$ values determined at low potential scan rates. The assignment of the corresponding oxidation states was based on related examples from the literature [4].

The difference of about 1 V between the successive redox potentials is quite significant, indicating a strong interaction between the ruthenium ions in the trinuclear centre.

In order to evaluate the role of the basicity of the N-heterocyclic ligands in the electrochemical behaviour of the trinuclear clusters, we carried out a careful determination of pK_a, under similar experi-

TABLE II. Formal Potentials of $[Ru_3O(OOCCH_3)_6(N\text{-}Het)_3]^{n/m}$ Redox Couples in Acetonitrile[a]

N-Het	pK_a[b]	−1/−2	0/−1	1/0	2/1	3/2
ampy	9.39		−1.35	−0.01	1.08	(2.0)
tbpy	6.14		−1.17	0.13	1.14	2.12
py	5.28		−1.13	0.15	1.19	2.14
py[c]			−1.08	0.19	1.21	2.17
adpy	3.59	(−1.4)	−0.98	0.19	1.21	2.16
acpy	3.60	(−1.1)	−0.87	0.24	1.25	2.19
mspy	3.48	−1.23	−0.90	0.22	1.25	2.20
ampz	3.05	(−1.4)	−0.93	0.23	1.25	2.10
dmpz	2.26	−1.36	−0.85	0.28	1.28	2.20
mpz[c]	1.50	−1.23	−0.79	0.34	1.35	2.32
pz	1.21	−1.22	−0.78	0.32	1.32	(2.2)

[a] V *versus* SHE, [TEAP] = 0.100 mol dm^3, 25 °C, estimated values in parentheses. [b] Aqueous solution, 25 °C, [KCl] = 0.100 mol dm^3. [c] Data from ref. 4, mpz = 2-methyl pyrazine.

mental conditions (25 °C, $I = 0.10$ mol dm^{-3} KCl), based on spectrophotometric measurements in the ultraviolet region. In all the cases, the plots of the Henderson–Hasselbalch equation were linear, with a slope = 1.0. The results are shown in Table II.

The redox potentials decrease linearly with the pK_a of the N-heterocyclic ligands, as one can see in Fig. 3. The variation is relatively small at high oxidation states, but increases rapidly as the oxidation states decrease, as expressed by eqns. (1)–(4).

$Ru^{IV}Ru^{IV}Ru^{III}/Ru^{IV}Ru^{III}Ru^{III}$ redox couples:

$$E^\circ \text{ (V } vs. \text{ SHE)} = 2.24\ (\pm 0.03) - 0.023\ (\pm 0.005)\ \mathrm{p}K_a \quad (1)$$

$Ru^{IV}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{III}$ redox couples:

$$E^\circ \text{ (V } vs. \text{ SHE)} = 1.34\ (\pm 0.01) - 0.029\ (\pm 0.002)\ \mathrm{p}K_a \quad (2)$$

$Ru^{III}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{II}$ redox couples:

$$E^\circ \text{ (V } vs. \text{ SHE)} = 0.36\ (\pm 0.01) - 0.039\ (\pm 0.002)\ \mathrm{p}K_a \quad (3)$$

$Ru^{III}Ru^{III}Ru^{II}/Ru^{III}Ru^{II}Ru^{II}$ redox couples:

$$E^\circ \text{ (V } vs. \text{ SHE)} = -0.68\ (\pm 0.04) - 0.074\ (\pm 0.006)\ \mathrm{p}K_a \quad (4)$$

The dependence of the redox potentials with the pK_a reflects the relative affinities of the oxidized and reduced metal ions for the coordinated ligands [9]. In general, as the pK_a of the ligand increases, the high oxidation states are stabilized, mainly via σ-bonding effects. This type of effect is responsible for the decrease of E° *versus* pK_a, in the case of the ruthenium(IV)/(III) redox couples. On the other hand, π-backbonding effects are expected to play an important role in the case of the ruthenium(III)/(II) redox couples, stabilizing the lowest oxidation state.

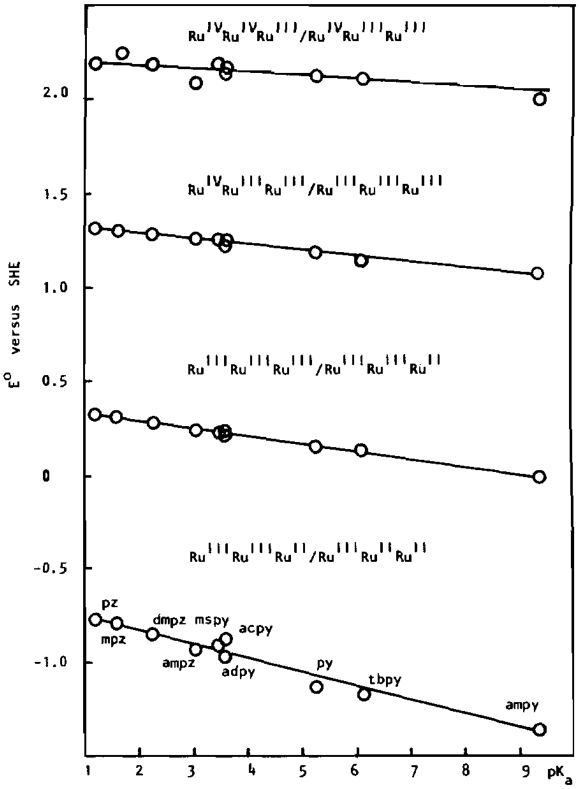

Fig. 3. Plots of the redox potentials of the $[Ru_3O(OOCCH_3)_6(N\text{-}Het)_3]$ clusters *vs.* the pK_a of the N-heterocyclic ligands.

According to the angular coefficients of eqns. (1) and (3), the effects of σ-bonding and π-backbonding are of comparable importance in the $Ru^{III}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{II}$ redox couples; however, in the case of the $Ru^{III}Ru^{III}Ru^{II}/Ru^{III}Ru^{II}Ru^{II}$ couples (eqn. (4)), the π-backbonding effects are at least two times more important. The trends extrapolated from eqns. (1)–(4) indicate that the redox potentials for the $Ru^{III}Ru^{II}Ru^{II}/Ru^{II}Ru^{II}Ru^{II}$ couples should be lower than −1.6 V *versus* SHE (expected value at $pK_a = 0$), exhibiting a great dependence with the pK_a. Although the measurements were limited, in most of the cases, by the working potentials in acetonitrile solutions, one can see that the available data for the −1/−2 couples in Table II do not follow the behaviour expected for the $Ru^{III}Ru^{II}Ru^{II}/Ru^{II}Ru^{II}Ru^{II}$ system. In the case of mixed complexes of the type $[Ru_3O(OOCCH_3)_6(py)_2L]$ where L = 4,4′ bipyridine, 1,2-bis(4-pyridyl)ethylene or pyrazine, the most cathodic redox wave has been ascribed to the reduction of the N-heterocyclic ligand L, usually observed around −1.5 V *versus* SHE [4]. Therefore, analogously to the preceding examples, the −1/−2 redox potentials in Table II would be better ascribed to the reduction of the N-heterocyclic ligands in the complexes.

In conclusion, the bonding properties of the N-heterocyclic ligands discriminate the several oxidation states of the trinuclear clusters, providing a useful way of tuning the redox levels for electron transfer purposes.

Acknowledgements

The support from CNPq, FINEP and FAPESP is gratefully acknowledged.

References

1 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1570 (1972).
2 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 786 (1974).
3 F. A. Cotton and J. G. Norman, *Inorg. Chim. Acta, 6,* 411 (1972).
4 J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer and W. E. Hatfield, *Inorg. Chem., 17,* 3342 (1978).
5 J. A. Baumann, D. J. Salmon, S. T. Wilson and T. J. Meyer, *Inorg. Chem., 18,* 2472 (1979).
6 J. A. Baumann, S. T. Wilson, D. J. Salmon, P. L. Hood and T. J. Meyer, *J. Am. Chem. Soc., 101,* 2916 (1979).
7 B. Kratochvil, E. Lorah and C. Garber, *Anal. Chem., 41,* 1793 (1969).
8 R. S. Nicholson and I. Shain, *Anal. Chem., 36,* 706 (1964).
9 D. A. Buckingham and A. M. Sargeson, in F. P. Dwyer and D. P. Mellor (eds.), 'Chelating Agents and Metal Chelates', Academic, Press, New York, 1964, p. 237.