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On the Electronic Structure of Tris(β-diketonato)ruthenium(III) Complexes: A Linear Correlation of Electrochemical Reduction Potentials in Solution with Vertical First Ionisation Energies in the Gas Phase

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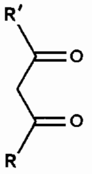
Tris(pentane-2,4-dionato)ruthenium(III), [Ru(acac)$_3$], was first reported in 1914 [1], and since that date several related [Ru(dik)$_3$] (dik = hfacac, dbzm, dnbzm, dpvm, bzac, tfacac or bztfac) complexes have been prepared in a number of separate studies [2]. However, as a series of structurally related molecules, these compounds have been largely ignored; the only detailed comparative study is that of Patterson and Holm [3]. Only [Ru(hfacac)$_3$] has been studied by photoelectron spectroscopy [4], and the two reports of the electronic absorption spectra of [Ru(acac)$_3$] [5, 6] differ significantly. We have prepared [Ru(dik)$_3$] (dik = acac, hfacac, tfacac, dpvm, dbzm, bzac and thtfac), and report here the crystal and molecular structure of *mer*-tris{1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato}ruthenium(III), the He I and He II photoelectron (PE) spectra of [Ru(dik)$_3$] (dik = acac, hfacac, tfacac, dpvm and thtfac), and discuss the relationships of the first ionisation energies of these molecules in the gas phase with their reduction potentials in solution and with the Taft and Hammett constants for the R,R′ substituents of the β-diketonato anion, [R′C(O)CHC(O)R]$^-$.



acacH: R = R′ = CH_3
hfacacH: R = R′ = CF_3
dbzmH: R = R′ = C_6H_5
dnbzmH: R = R′ = C_6H_4-4-NO_2
dpvmH: R = R′ = CMe_3
bzacH: R = C_6H_5, R′ = CH_3
tfacacH: R = CF_3, R′ = CH_3
bztfacH: R = C_6H_5, R′ = CF_3
thtfacH: R = 2-C_4H_3S, R′ = CF_3

The seven [Ru(dik)$_3$] complexes were prepared by minor modifications of standard literature routes [2], and were characterised by IR, ^{1}H and ^{19}F NMR, and electronic absorption spectroscopy, cyclic voltammetry, mass spectrometry and microanalysis. The crystal and molecular structures were solved for a single crystal* of *mer*-tris{1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dionato}ruthenium(III), and the molecular structure is illustrated in Fig. 1. Perhaps the most interesting feature of this structure is that $\bar{r}$(RuO), at 0.200(1) nm, is identical to that found in [Ru(acac)$_3$] [7], despite the electronic asymmetry inherent in the [thtfac]$^-$ ligand. Moreover, although the molecule is of low formal symmetry, the {RuO_6} core approximates well to an octahedral geometry,

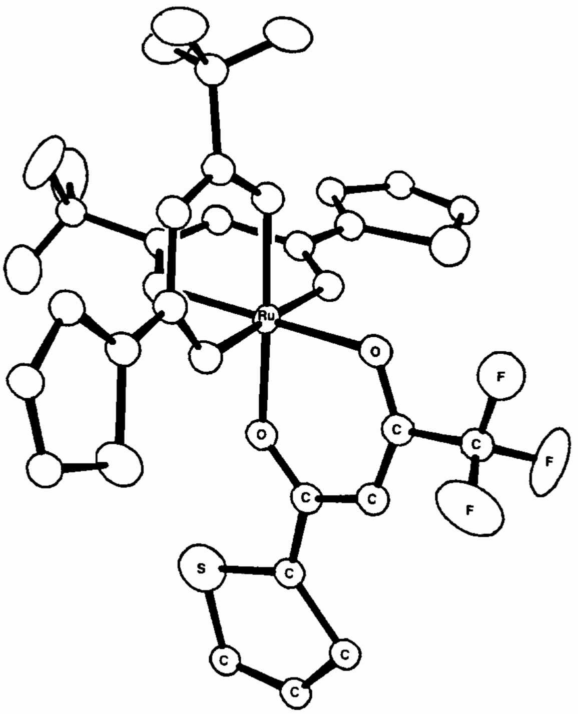


Fig. 1. The molecular structure of *mer*-[Ru(thtfac)$_3$].

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*Crystal data: $C_{24}H_{12}F_9O_6RuS_3$, M_r = 764.61, monoclinic space group $P2_1/n$, a = 1.3843(5), b = 1.3860(5), c = 1.5166(4) nm, β = 102.66(2)°, U = 2.8391 nm^3, Z = 4, D_c = 1.79 g cm^{-3}, μ(Mo Kα) = 8.6 cm^{-1}, crystal dimensions = 0.35 × 0.10 × 0.23 mm. The data were measured on an Enraf-Nonius CAD4 diffractometer. 1937 reflections were used in the refinement, which converged at R = 0.088, R' = 0.074. For atomic coordinates see 'Supplementary Material'.

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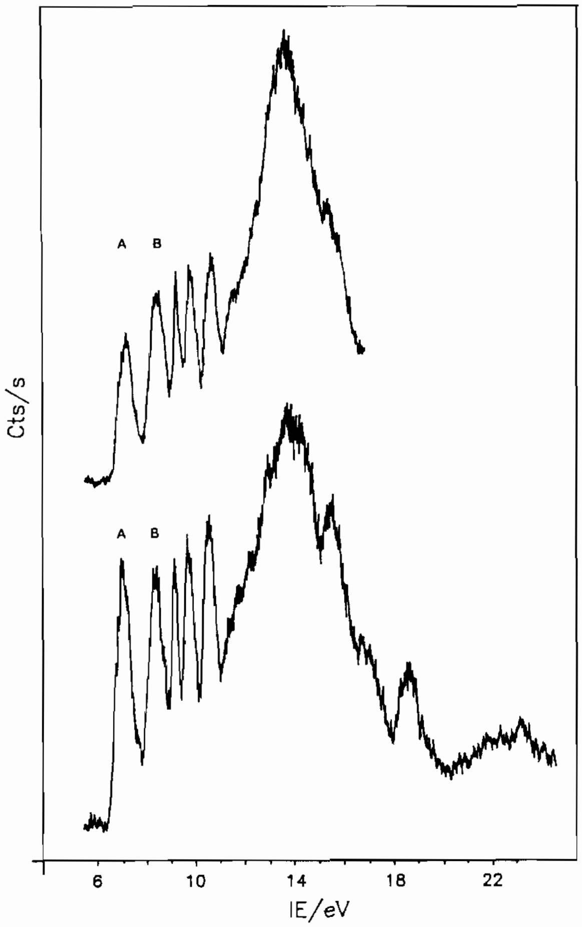

Fig. 2. The He I (upper) and He II (lower) gas-phase photoelectron spectra of [Ru(acac)$_3$].

thus allowing the electronic structure to be discussed in terms of a $(t_{2g})^5$ configuration.

The five volatile complexes were studied by photoelectron spectroscopy, and the He I and He II spectra of [Ru(acac)$_3$] are depicted in Fig. 2. [Ru(tfacac)$_3$], [Ru(hfacac)$_3$] and [Ru(dpvm)$_3$] exhibit similar spectral profiles, but the spectra of [Ru(thtfac)$_3$] are complicated by the presence of sulfur lone-pairs associated with the heterocyclic ring. The increase in intensity of band A relative to band B on changing from He I to He II ionising radiation unambiguously identifies band A with the essentially non-bonding $(t_{2g})^5$ metal-based electrons. These vertical first ionisation energies of the complexes were found to correlate linearly with their reduction potentials in *N,N*-dimethylmethanamide solution (see Fig. 3). Although linear correlations between the first ionisation energies and oxidation potentials of several series of related molecules have been demonstrated [e.g. 8–10] and theoretically justified, hitherto reduction potentials have been related to electron affinities. The complexes [Ru(dik)$_3$], however, are open shell molecules {with an electronic configuration approximating to [core]$(t_{2g})^5$ (*vide supra*)}, implying that electrochemical reduction of these complexes directly involves the HOMO. We believe this to be the first observation of such a correlation. Moreover, the first ionisation potentials of these molecules, as well as their first reduction potentials, correlate well (see Fig. 4) with the sum of the one-ligand Taft polar substituent parameters ($\sigma_R{}^* + \sigma_{R'}{}^*$) [11, 12], which gives a rather better linear fit to the experimental data than correlation with either of the Hammett constants (σ_m or σ_p).

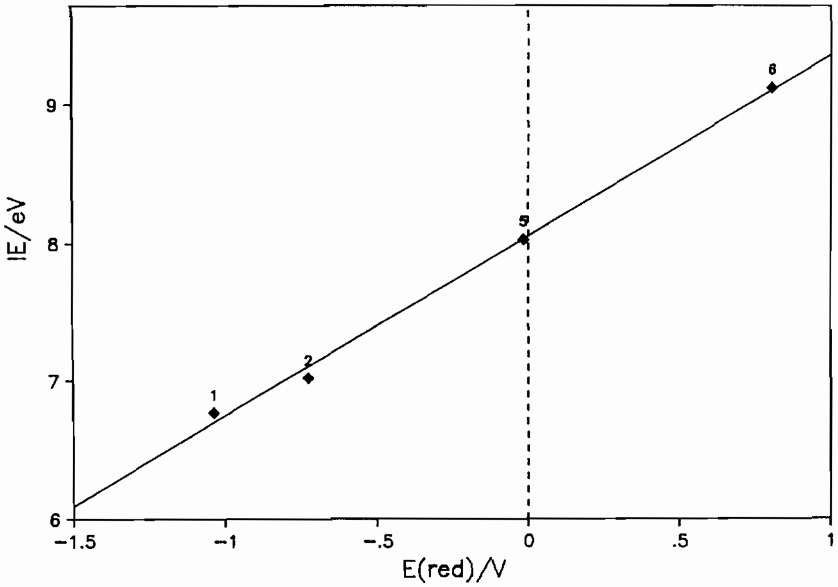

Fig. 3. Correlation of the first vertical gas-phase ionisation energy with the first reduction potential (in *N,N*-dimethylmethanamide solution, *vs.* SCE [3]) for (1) [Ru(dpvm)$_3$], (2) [Ru(acac)$_3$], (5) [Ru(tfacac)$_3$] and (6) [Ru(hfacac)$_3$].

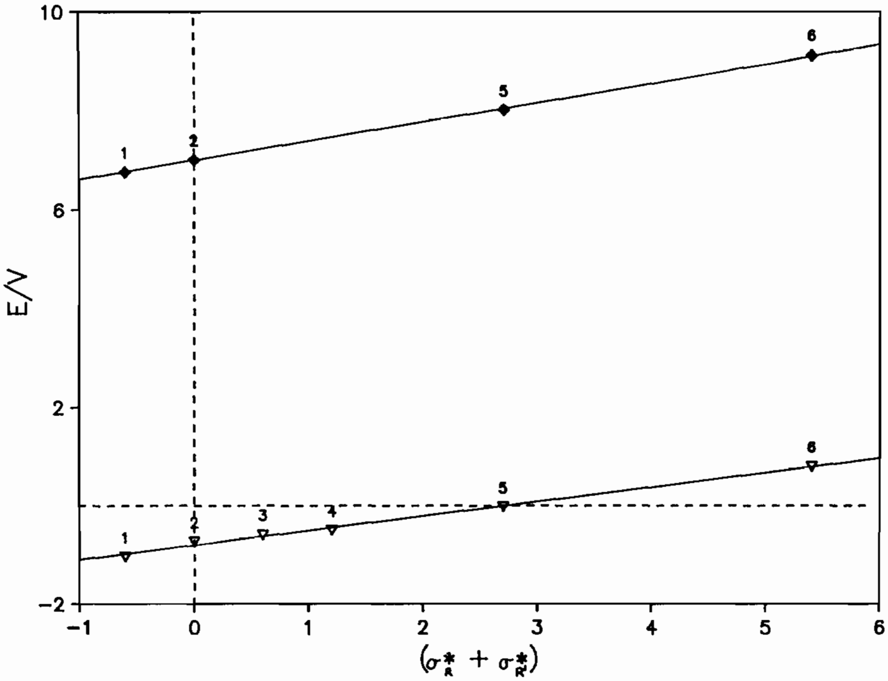

Fig. 4. Correlation of the first vertical gas-phase ionisation energy (◆; units of eV) and the first reduction potential (▽; in *N,N*-dimethylmethanamide solution, *vs.* SCE [3]) with the sum of the one-ligand Taft polar substituent parameters (σ_R^* + $\sigma_{R'}^*$) for (1) $[Ru(dpvm)_3]$, (2) $[Ru(acac)_3]$, (3) $[Ru(bzac)_3]$, (4) $[Ru(dbzm)_3]$, (5) $[Ru(tfacac)_3]$, and (6) $[Ru(hfacac)_3]$.

Supplementary Material

The atomic coordinates for this work are available on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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