J. Chem. Soc., Faraday Trans. 1, 1989, **85**(12), 4047–4052

Binuclear Radical Complexes of Heavy-metal Fragments containing Ruthenium, Osmium, Rhodium and Gold

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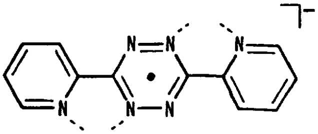
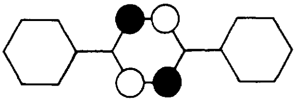
Homobinuclear chelate complexes of the 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine anion radical ligand with the metal fragments $[Os(bpy)]^{2+}$ (d^6), $[Rh(norbonadiene)]^+$ (d^8) and $[Au(PPh_3)]^+$ (d^{10}) have been studied by ESR spectroscopy. The unique suitability of this radical ligand for coordination of heavy metal fragments and for ESR investigations is discussed.

Paramagnetic complexes of the precious metals are scarce mainly for two reasons: metals of the 4d and 5d series in the periodic table are notorious for avoiding configurations with an odd number of d electrons,[1] thus corresponding more to main-group element analogues. A second possibility, the coordination of such metals in their stable d^{2n} configurations to the generally nucleophilic anion radical ligands,[2,3] often fails because of the facile reducibility of ionized precious metal centres to the elements. Using the negatively charged 'spin label ligand'[4] 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine radical anion ($bptz^{\cdot-}$, 1)[5–7] we have been able to generate and characterize by ESR the first binuclear radical complexes of osmium(II), rhodium(I) and gold(I).



(1)



(2)

The radical anion ligand (**1**) is perfectly suited for the stabilization and ESR characterization of metal centres.[5–7] It offers (i) two identical chelate coordination sites, each with one basic pyridyl 'anchor', (ii) a less negative reduction potential of −0.72 V *vs.* SCE which can be further increased considerably by metal coordination,[5] (iii) an extremely high disproportionation constant for the radical anion intermediate,[5] (iv) a very simple ESR hyperfine splitting due to a nodal plane through the tetrazine 3, 6-positions in the singly occupied MO (2),[5,6] (v) large spin densities on the coordinating tetrazine nitrogen atoms which cause relatively large metal (isotope) coupling of the two equivalent coordinated metal fragments.[5,6] Furthermore, the structure and electronic spectrum of one complex, a copper(I) dimer, have been determined and interpreted.[8]

Reported examples include complexes of $bptz^{\cdot-}$ with $[Ru(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine),[6] $[(R_3P)_2Cu]^+$,[9] (cod)Cu^+ (cod = 1,5-cyclo-octadiene),[9] $(OC)_4M$ (M = Cr, Mo, W),[5] and $(OC)_3XRe$ (X = Cl, Br).[7] We now describe the synthesis and ESR characteristics (fig. 1–3, table 1) of $\{(bptz)[Os(bpy)_2]_2\}^{\cdot 3+}$, $\{(bptz)[Rh(nbd)]_2\}^{\cdot +}$ (nbd = norbornadiene), and of $\{(bptz)[Au(PPh_3)]_2\}^{\cdot +}$.

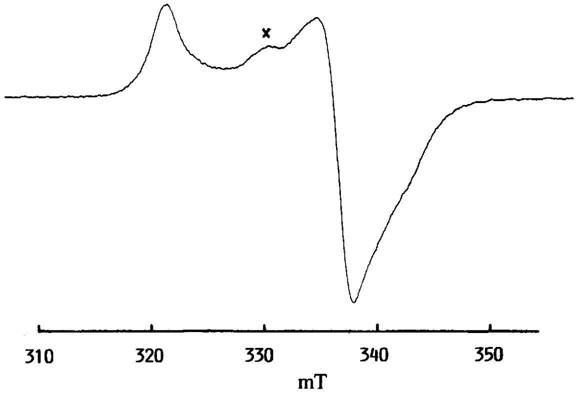


Fig. 1. ESR spectrum of $\{(bptz)[Os(bpy)_2]_2\}^{\cdot 3+}$ in frozen acetone at 3.8 K. × marks an impurity.

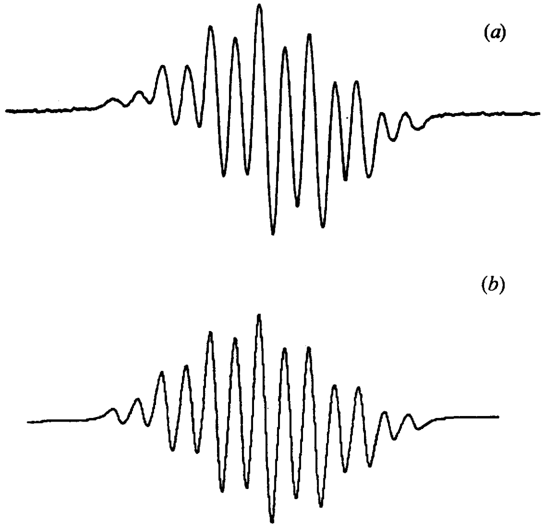


Fig. 2. (*a*) ESR spectrum of $\{(bptz)[Rh(nbd)]_2\}^{\cdot +}$ in dichloromethane at 300 K; (*b*) computer simulation with the data from table 1.

Experimental

ESR spectra were recorded in the X-band on Varian E9 and 109 spectrometers. *g* Factors and coupling constants were determined either by use of the double-cavity technique with perylene radical anion as reference[5,6] or by directly measuring magnetic field and microwave frequency (Varian NMR gaussmeter, EIP 548A frequency counter). Liquid-helium temperatures were generated using an Oxford Instruments ESR 900 cryostat.

The synthesis of the bptz ligand has been described previously.[5,6] The red binuclear osmium radical complex was obtained by reduction of $\{(bptz)[Os(bpy)_2]_2\}(PF_6)_4$[10] with tetrabutylammonium tetrahydridoborate in acetone solution; however, an ESR spectrum was observed only at very low temperatures.

The binuclear rhodium radical complex was generated by adding 1 mg of bptz and 10 mg of $[Rh(nbd)Cl]_2$ in 3 cm^3 dichloromethane, followed by reduction with zinc powder.

The paramagnetic gold dimer was obtained in the following way: triphenylphosphanegold chloride (50 mg, 0.1 mmol) was dissolved in 30 cm^3 methanol and

Table 1. ESR data[a] of binuclear complexes with the bptz anion radical and metal isotope characteristics

metal fragment	a_N[b]	a_N[c]	Δa_N	metal isotope	$A_{iso}(M)$[d]	a_M	$10^3\, a_M/A_{iso}$	g	λ_M[e]	ref.
$\mathrm{Cr^{\circ}(CO)_4}$	0.459	0.622	0.163	^{53}Cr	−22.5	0.11	4.88	2.0033	223	5
$\mathrm{Mo^{\circ}(CO)_4}$	0.420	0.640	0.220	^{95,97}Mo	−47.1	0.230	4.88	2.0045	552	5
$\mathrm{W^{\circ}(CO)_4}$	0.415	0.640	0.225	^{183}W	53.6	0.415	7.74	2.0068	2089	5
$\mathrm{^{+}Cu^{I}(cod)}$	0.415	0.683	0.267	^{63,65}Cu	183.0	0.960	5.25	2.0053	828	9
$\mathrm{^{+}Cu^{I}(PPh_3)_2}$	0.463	0.605	0.142	^{63,65}Cu	183.0	0.758	4.14	2.0055	828	9
$\mathrm{^{+}Cu^{I}(diphos)}$	0.442	0.624	0.182	^{63,65}Cu	183.0	0.936	5.11	2.0058	828	9
$\mathrm{^{+}Au^{I}(PPh_3)}$	0.37[j]	0.74[j]	0.37	^{197}Au	31.3	<0.1	<3.2	2.0073	5091	this work
$\mathrm{^{+}Rh^{I}(nbd)}$	0.33[k]	0.66[k]	0.33	^{103}Rh	−28.6	<0.07	<2.5	2.0062	1212	this work
$\mathrm{^{2+}Ru^{II}(bpy)_2}$	0.55[f]	0.55[f]	*f*	^{99,101}Ru	−39.6	0.45	11.36	1.9980	990	6
$\mathrm{^{2+}Os^{II}(bpy)_2}$	*g*	*g*	*g*	^{189}Os	118.3	*g*	*g*	1.9865[i]	*ca.* 2500	this work
$\mathrm{Re^{I}(CO)_3Cl}$	*h*	*h*	*h*	^{185,187}Re	320.0	2.2	6.87	2.0051	2200	7
—	0.495	0.495	0	—	—	—	—	2.0040	—	5

[a] Coupling constants in mT. Estimated error ±0.005 mT, except when noted otherwise. [b] Non-coordinating nitrogen centres. [c] Coordinating tetrazine nitrogen centres. [d] Isotropic hyperfine coupling constant of metal isotope M [from ref. (1)]. [e] Spin–orbit coupling constant (in $\mathrm{cm^{-1}}$). [f] Not accurately determined, possible error ±0.15 mT. [g] No hyperfine coupling detected in low-temperature spectrum. [h] Not resolved. [i] Isotropic value calculated from $g_\perp = 1.9609$ and $g_\parallel = 2.0366$. [j] Estimated error ±0.1 mT. [k] Estimated error ±0.05 mT.

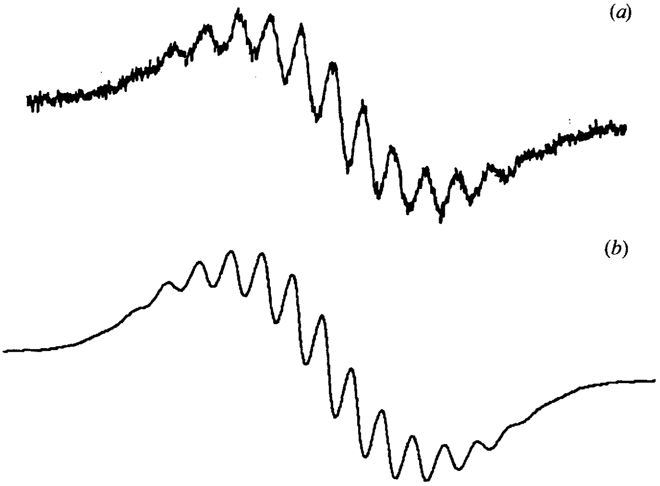


Fig. 3. (*a*) ESR spectrum of $\{(\text{bptz})[\text{Au}(\text{PPh}_3)]_2\}^{\bullet +}$ in dichloromethane at 300 K; (*b*) computer simulation with the nitrogen coupling constants from table 1, $a(^{31}\text{P}) = 0.37$ mT (2P) and 0.38 mT linewidth.

treated with 20 mg (0.1 mmol) of silver tetrafluoroborate. After removal of precipitated AgCl, the filtrate was evaporated to dryness and redissolved in 50 cm^3 dichloromethane/methanol (5:1) together with 10 mg (0.04 mmol) bptz. This mixture was reduced for 16 h with zinc powder and the paramagnetic solution used for ESR measurement.

Results

The red paramagnetic osmium dimer was obtained by reduction of the blue–green diamagnetic tetracation[10] with BH_4^- in acetone. In contrast to the ruthenium analogue[6] it does not exhibit an ESR signal at 300 K but only after cooling to very low temperatures (fig. 1). This effect has previously been noted for complexes of $[\text{Ru}(\text{bpy})_2]^{2+}$ with the extremely π-accepting azodicarboxylic esters (adc),[11] and it signifies very strong metal–ligand interactions and significant contributions from metal d orbitals to the singly occupied MO. The similar behaviour of the Ru/adc and Os/bptz systems is compatible with a more destabilized +II oxidation state for the heavier metal.[12] The rhombic signal found in a glassy matrix (fig. 1) shows a larger *g* anisotropy than that measured for the ruthenium analogue; this is a consequence of the higher spin–orbit coupling constant of osmium (table 1).[1,13]

The dirhodium radical was obtained by treating bptz and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ with reducing zinc metal in dichloromethane. A well resolved ESR spectrum is obtained (fig. 2); the increased *g* value and the ratio of the two ^{14}N coupling constants of the tetrazine nitrogen centres are indicative of considerable perturbation by metal coordination.[5,6] A ^{103}Rh splitting ($I = \frac{1}{2}$, 100%) was *not* observed and must be smaller than 0.07 mT, the isotropic hyperfine coupling constant A_{iso} of this isotope is rather small indeed (table 1).[1] Incidentally, a poorly resolved ESR signal of a mononuclear radical complex $[(\text{bpy})\text{Rh}(\text{nbd})]^{\bullet}$ had been reported previously.[14]

The paramagnetic gold dimer, the first radical complex of gold after a few silver(I) semiquinone species were reported,[15] was obtained by treating bptz and ClAuPPh_3 first with AgBF_4 to remove the halide and then with zinc in dichloromethane. Triphenylphosphinegold cation is a rather inert and less reducible electrophile[16] which can coordinate in a semi-chelating fashion to α-di-imines such as bpy.[17] The relatively large

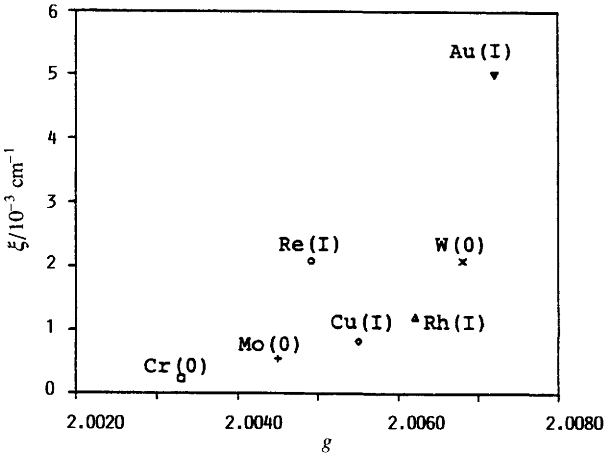


Fig. 4. Correlation between g factors of binuclear bptz radical anion complexes and the spin–orbit coupling constants ξ of coordinating metal centres.

isotropic g indicates the presence of coordinated heavy-metal centres with large spin–orbit coupling constants (table 1).[1,2,5,18] Assuming reasonable magnitudes of the two nitrogen coupling constants from the tetrazine rings[5–7,9] it is just a triplet from two ^{31}P nuclei ($I = \frac{1}{2}$, 100%) that is required to achieve a satisfactory computer-simulated spectrum (fig. 3). Whereas the coupling $a(^{31}P)$ is large for the PPh$_3$ co-ligands in the related bis(phosphane)copper(I) complex with tetrahedrally disposed metal,[8,9] the small phosphorus coupling observed here is more compatible with the expected coplanar arrangement π ligand/Au/P.[17] Similarly small coupling constants $a(^{31}P)$ have been reported for phosphorus centres in the MO nodal planes of a phosphaheterocycle[19] and of a P$_6$-bridged triple-decker complex.[20] The ^{195}Au metal coupling ($I = \frac{3}{2}$, 100%) could not be detected and the A_{iso} value of this isotope is similarly small, of the order of that of ^{103}Rh (table 1).[1]

Discussion

The data in table 1 illustrate that the sum of the tetrazine N splittings remains fairly constant with $a_N + a_{N'} = 1.05 \pm 0.08$ mT; at least 90% of the total spin density is concentrated on these four centres.[5] The difference between the two coupling constants for coordinated and non-coordinated tetrazine centres varies with the extent of perturbation by the metal and shows a maximum at intermediate values.[5,6] Apparently, this maximal difference occurs for the rhodium and gold complexes described here. Stronger perturbation, *e.g.* by the dipositive ruthenium centres, results in less disparate tetrazine N coupling constants.[6] The free-anion radical ligand displays only one coupling constant for all four tetrazine nitrogen centres, which indicates free rotation of the pyridyl group; the bond order between the rings is not sufficiently increased upon reduction because of the π MO nodal plane through centres 3 and 6 of the tetrazine.[5]

Metal coupling constants are dependent on the nature of the co-ligands as is illustrated by the copper(I) systems;[9] nevertheless, the ratio a/A_{iso} does show some significant variation from very small values for the presumably planar rhodium(I) and gold(I) centres to the large a/A_{iso} for the ruthenium(II) complex with its rather strong metal–ligand interaction.[6] Osmium isotope coupling (^{189}Os: $I = \frac{3}{2}$, 16.1% natural abundance) could not be observed in the low-temperature spectrum (fig. 1); an expected $a(^{189}Os)$ of *ca.* 1 mT should not be easily seen in view of the linewidth and of the low probability of 2.6% for the combination with two ^{189}Os isotopes (the combination with one active isotope has 27% probability).[2,18]

The isotropic *g* factors of most of the radical complexes in table 1 show a correlation with the spin–orbit coupling factors of the coordinated metal centres (fig. 4). This is expected[2,18] in the absence of interfering co-ligands, *e.g.* with unusually low-lying relevant molecular orbitals.[6,21] The deviation of the rhenium chloride system[7] (fig. 4) and the strong deviations of bis(bipyridine)-ruthenium and -osmium complexes are in fact due to low-lying unoccupied π^* (bpy) or σ^* (Re—Cl) orbitals, and the *g* factors of these systems are unusually small, in agreement with theory.[2,6,21]

Results from ESR spectroscopy on the molecular orbital situation in complexes can be useful in understanding electro- and photo-chemical reactivity.[7,22,23] The unique properties of the bptz radical anion ligand should thus be further explored with other metal fragments in order to gain an understanding of the metal–ligand interaction.

This work was generously supported by Deutsche Forschungsgemeinschaft and by Stiftung Volkswagenwerk. We thank Dr J. Jordanov and the C.E.N.G. (Grenoble, France) for the opportunity to perform low-temperature ESR studies.

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Paper 9/01602C; *Received* 17*th April*, 1989