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Calcium and strontium, and zinc (phenazine)$^{-}$• species

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Abstract

Calcium and strontium react with phenazine in tetrahydrofuran (THF) at ca 20 °C to yield red solutions containing paramagnetic species based on (phenazine)$^{-}$• (ESR characterization). Zinc reacts in THF in the presence of zinc chloride or bromide, or without metal halide in pyridine, to yield green or red ESR-active solutions also based on (phenazine)$^{-}$•, and then, for the reaction in pyridine, a brown paramagnetic solid of composition Zn(phenazine)(pyridine)$_2$.

While electron transfer reactions of Group 1 metals with polycyclic $(4n+2)\pi$ aza compounds are well documented [1] there have been only a few studies on Group 2 elements [2–4], and to our knowledge only one on the Group 12 elements [5]. Magnesium metal and phenazine in THF (tetrahydrofuran) yield a radical anion species, and then, in the presence of magnesium bromide, a dianion-containing compound [3] in a process somewhat similar to the important reaction of the isolobal anthracene with magnesium [6]. We have now found that (i) calcium and strontium also react with excess phenazine in THF; (ii) zinc reacts in THF only in the presence of zinc halides; and (iii) zinc and phenazine react directly in pyridine to yield a compound of composition Zn(phenazine)(pyridine)$_2$.

The results are summarized in Scheme 1. Sonication [7] in THF at room temperature of activated Ca derived from condensation of metal vapour in hexane, or of Sr chips gave red ESR-active solutions, Table 1. Over several days all the metal dissolved, with deposition of THF-free brown solids of variable composition and ESR-active, with broad featureless singlets close to the g_{av} value of 2.0032. Barium gave a similar paramagnetic product but without formation of a detectable ESR-active species in solution. No reaction was evident between phenazine and activated zinc powder (sonication in THF with 1,2-dibromoethane, followed by washing with freshly distilled THF), but in the presence of zinc chloride or bromide green solutions containing persistent radicals (Table 1) were formed, and this was followed by separation of a green precipitate, again of variable composition. Replacing

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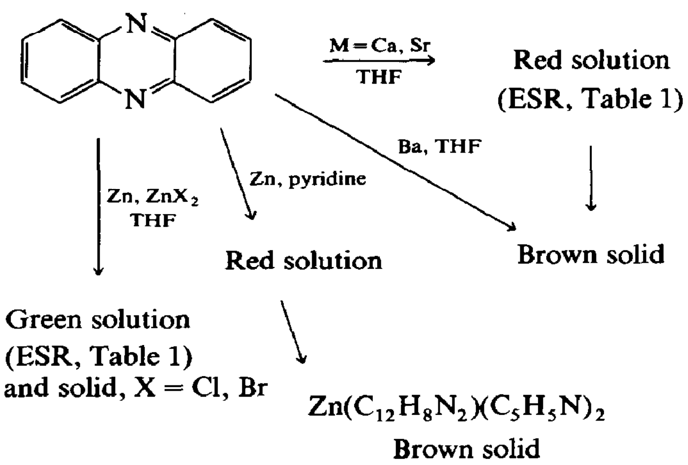

Scheme 1

Table 1

ESR data for Ca, Sr and Zn phenazine radical anion species in THF at ca 20°C

Metal	g_{av}	a_N [a]	a_H
Ca	2.0031	0.679, 0.363	0.229(4H), 0.084(4H)
Sr	2.0013	0.573, 0.456	0.233(4H), 0.100(4H)
Zn [b]	2.0045	0.619(2N)	0.253(2H), 0.146(H) 0.096(4H)
Zn [c]	2.0034	0.656, 0.584	0.181(4H),0.125(2H), 0.072(2H)

[a] Coupling constants in mT, line widths 0.05–0.08 mT. [b] Results with zinc chloride present. [c] Results with zinc bromide present.

the solvent with pyridine removed the need for metal halide, and a brown solid of composition Zn(phenazine)(pyridine)$_2$ * was formed (broad featureless ESR spectrum, g_{av} 2.0043) from a red ESR-active solution (complex spectrum). The solid does not contain coupled pyridines, which are often formed on reaction of pyridine with metals, and may contain the radical anions of both phenazine and pyridine. Cadmium and mercury did not react with phenazine in THF even in the presence of metal(II) chlorides, although $HgCl_2$, Hg, and phenazine gave Hg_2Cl_2 (97%). In the absence of phenazine this conproportionation does not occur, and so phenazine seemingly acts as an electron-carrier catalyst.

Simulated spectra for the hyperfine coupling values in Table 1 are in close agreement with those observed (Fig. 1). The low abundance of spin-active isotopes

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* The ^1H NMR spectra on material formed after quenching with CCl_4 or $CDCl_3$ showed that the complexes formed in THF were free of solvent, and revealed a ratio of phenazine to pyridine at 1 : 2 for the zinc compound formed in pyridine. The IR spectra on all species containing Zn, Ca, Sr, or Ba showed ν(CC) and ν(NC) bands close to 1575 cm^{-1} (cf. 1632 cm^{-1} for phenazine) and a band at 800 cm^{-1}. Microanalysis for Zn(phenazine)(pyridine)$_2$: found C, 64.4; H, 4.65; N, 12.1; Zn, 15.6%. $C_{22}H_{18}N_4Zn$ requires C, 65.44; H, 4.49; N, 13.87; Zn, 16.19%.

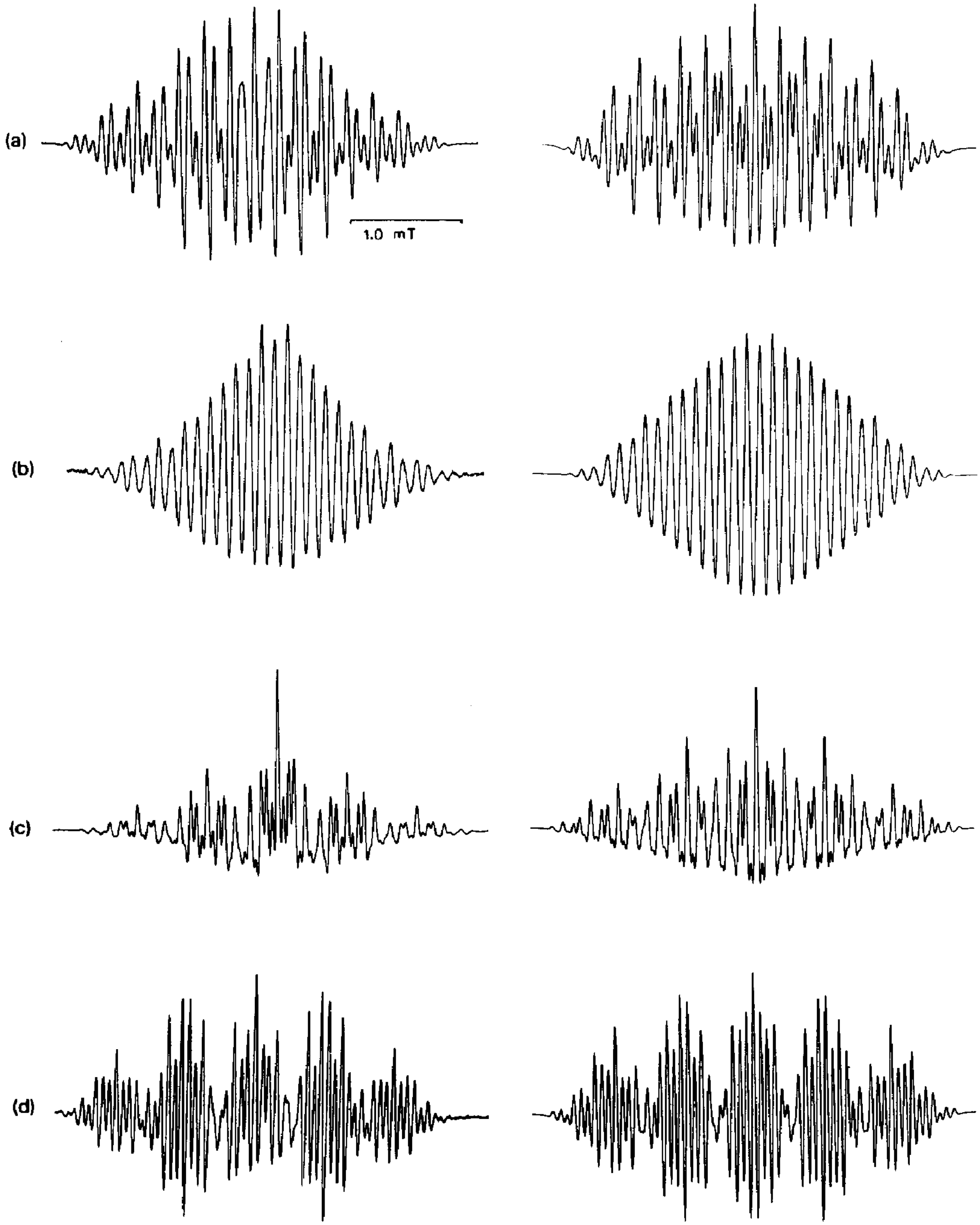

Fig. 1. Observed and reconstructed ESR spectra based on hyperfine coupling constants in Table 1 for radical anions derived from phenazine in THF with (a) calcium, (b) strontium, (c) zinc/zinc chloride, and (d) zinc/zinc bromide (sweep width 4.0 mT).

of the metals studied (^{43}Ca 0.14% $I_{7/2}$, ^{87}Sr 7.0% $I_{9/2}$, ^{135,137}Ba 6.6, 11.2% $I_{3/2}$, ^{67}Zn 4.1% $I_{5/2}$) made assignment of any hyperfine metal coupling constants difficult, and no coupling to high abundant spin-active isotopes of bromine or chloride was evident. The splitting patterns in the spectra for calcium and strontium are made up of two triplets from two different nitrogens and two quintets from two sets of four equivalent protons. The presence of two different nitrogens suggests that the metal centres are bound to only one of the N-centres of the radical anion of phenazine; the greater asymmetry of the Ca^{2+} species is consistent with a greater charge density for the slightly smaller Ca^{2+} ion than of Sr^{2+}, which results in stronger binding to nitrogen. The presence of two different N-centres, however, seems to be in conflict with the coupling to the protons, which is to two sets of four equivalent protons. In the case of the zinc halide phenazine species there are one or two different couplings to nitrogen but with coupling to one set of four equivalent nuclei, the remaining coupling being to two sets of two equivalent nuclei, as in phenazine mono-*N*-oxide [7]. The species present in THF for Ca and Sr, and in pyridine for Zn, are possibly of the type $M(phenazine)_2(solvent)_n$ formed through electron transfer in the presence of excess phenazine. It is noteworthy that for the potassium radical anion of phenazine, for which N-complexation is less likely, the coupling is symmetrical (a_N 0.514 mT, a_H 0.193 mT, a_H 0.161 mT) [9]. The primary process involving zinc metal/zinc halide presumably involves electron transfer at the metal surface to phenazine activated by complexation with zinc halide.

All the Group 2 and zinc phenazine containing solids have low solubilities in organic solvents, and are likely to have polymeric structures with high ionic character for the heavier Group 2 elements. They are rapidly oxidized in air to give purple phenazahydrin then phenazine, and can in principle act as sources of activated metal with organic substrates, as do magnesium(anthracene) complexes [10]. In this connection we have established that $Zn(phenazine)(pyridine)_2$/ethyl bromoacetate/cyclohexanone in THF affords the Reformatsky product in ca 30% yield.

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