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Synthesis and coordination chemistry of a water-soluble verdazyl radical. structures and magnetic properties of $M(H_2O)_2(vdCO_2)_2{\cdot}2H_2O$ (M = Co, Ni; $vdCO_2$ = 1,5-dimethyl-6-oxo-verdazyl-3-carboxylate)

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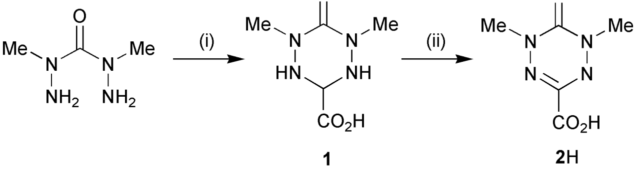
The synthesis of a verdazyl radical with a carboxylate substituent renders the radical highly soluble in water, thereby permitting the aqueous synthesis of Ni(II) and Co(II) verdazyl complexes which have been structurally and magnetically characterized.

Metal complexes of coordinated radicals have attracted a great deal of attention for their intrinsically interesting electronic structures, biological importance, and in particular as potential building blocks for hybrid metal–organic magnetic materials.[1–5] Most stable radicals that can be employed as ligands are either unstable or insoluble in water, thereby limiting coordination chemistry to non-aqueous media. As part of our ongoing program focusing on transition metal complexes of verdazyl radicals,[6] herein we present the synthesis and preliminary molecular coordination chemistry of a verdazyl radical bearing a simple carboxylic acid group—the deprotonated form of which is freely soluble in water and other polar solvents, opening up new preparative avenues in *aqueous* metal–radical chemistry.

The title radical was prepared as shown in Scheme 1. The condensation reaction of carbonic acid bis(1-methyl hydrazide)[7] with glyoxilic acid afforded tetrazane **1** in near quantitative yield. Oxidation of the tetrazane with benzoquinone gave verdazyl-3-carboxylic acid **2**H as a maroon solid. The radical has been fully characterized in both the protonated (carboxylic acid, **2**H) and deprotonated (carboxylate, **2**$^-$) forms. The protonated form of the radical **2**H is only sparingly soluble in all solvents, but the carboxylate form **2**$^-$ is highly soluble in water. The EPR spectrum of **2**H is typical of 1,5-dimethyl-6-oxoverdazyl derivatives, showing hyperfine coupling to the four heterocyclic nitrogen atoms ($a(N_1) = 6.5$ G (2N) and $a(N_2) = 5.3$ G (2N) as well as the six methyl protons ($a(H) = 5.3$ G). Full details of the synthesis, structure and solid state magnetic properties of the radical anion **2**$^-$ will be published elsewhere.

We have begun to explore the coordination chemistry of verdazyl **2**$^-$ with M^{2+} salts. Reaction of **2**H with either nickel or cobalt chlorides or perchlorate salts in basic aqueous solution leads to immediate precipitation of the metal complexes of formula $M(H_2O)_2(\mathbf{2})_2{\cdot}2H_2O$ (**3**, M = Ni; **4**, M = Co). Single crystals of these materials were grown by allowing solutions of the tetrazane **1** and M^{2+} in aqueous base to stand in air for several days.† This behaviour has been reported for other verdazyl metal complexes[8] and may involve metal-catalyzed air oxidation of the tetrazane to the verdazyl, since the same process carried out under inert atmosphere leads only to intractable mixtures. The spectroscopic and analytical data for the complexes made by both routes are identical.



Scheme 1 *Reagents and conditions*: (i) glyoxilic acid, H_2O, 0.5 h, r.t. 96%; (ii) *p*-benzoquinone, EtOAc/MeOH, 1.5 h, 45 °C, 54%.

The X-ray crystal structures‡ of the Ni and Co complexes were determined. An ORTEP drawing of the Ni complex **3** is shown in Fig. 1; The corresponding Co complex is isostructural. Both complexes consist of a pseudo-octahedral metal(II) ion containing two *trans* aquo ligands in axial positions and two verdazyl ligands bound to the metal in the equatorial plane in an *N*,*O*-chelating mode. The *anti* orientation of the two chelating ligands confers approximate C_{2h} symmetry upon the molecule. There are also two non-coordinated water molecules in the lattice. The bond lengths and angles within each radical are typical for coordinated verdazyls, and the Ni–N bond lengths in **3** are comparable to those found in another Ni(II) verdazyl complex.[10] Structure **4** represents the first cobalt complex containing a coordinated verdazyl radical.

The temperature dependence of the magnetic susceptibility of **3** and **4** have been measured from 2 to 300 K. The results are presented in the form of χT *vs.* T plots (Fig. 2). For the Ni complex **3**, the room temperature value of χT (2.63 emu K mol^{-1}) is significantly higher than the expected value (1.96 emu K mol^{-1}, assuming $g_{\mathrm{rad}} = 2$ and $g_{\mathrm{Ni}} = 2.2$) for an uncorrelated $S = 1$ plus two $S = 1/2$ spin system. The χT product steadily increases as the temperature is lowered, reaching a maximum at 80 K. The χT product then begins to decreas and then drops rapidly below 20 K from a combination of intermolecular antiferromagnetic interactions and/or zero-field splitting of the high-spin nickel(II). The χT data for **3** were simulated using a spin Hamiltonian of the form $\boldsymbol{H} = -2J_{\mathrm{Ni-vd}}(\boldsymbol{S}_{\mathrm{vd1}}\boldsymbol{S}_{\mathrm{Ni}} + \boldsymbol{S}_{\mathrm{vd2}}\boldsymbol{S}_{\mathrm{Ni}}) - 2J_{\mathrm{vd-vd}}\boldsymbol{S}_{\mathrm{vd1}}\boldsymbol{S}_{\mathrm{vd2}}$, where $\boldsymbol{S}_{\mathrm{Ni}} = 1$ and $\boldsymbol{S}_{\mathrm{vd1}} = \boldsymbol{S}_{\mathrm{vd2}} = \frac{1}{2}$. Because of the large number of parameters in this spin system it was necessary to fix some of the parameters at sensible values. Thus, typical *g*-values were set for the radical ($g_{\mathrm{vd}} = 2.0$) and the Ni(II) ion ($g_{\mathrm{Ni}} = 2.2$) and the best fit produced the following

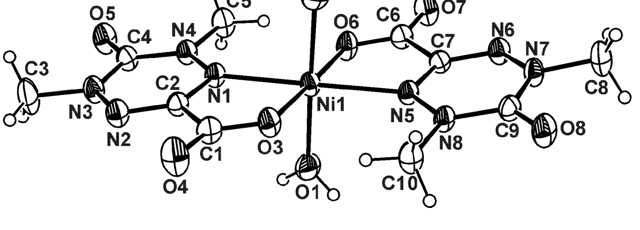


Fig. 1 ORTEP Drawing of $Ni(H_2O)_2(\mathbf{2})_2{\cdot}2H_2O$ **3** (35% ellipsoids). Non-coordinated water molecules not shown. Selected bond lengths (Å): Ni1–N1 2.185(18), Ni1–N5 2.192(18), Ni1–O1 2.037(17), Ni1–O2 2.097(16), Ni1–O3 2.055(17), Ni1–O6 2.043(17). Selected bond lengths (Å) for corresponding Co complex **4**: Co1–N1 2.127(2), Co1–N5 2.141(2), Co1–O1 2.023(2), Co1–O2 2.060(2), Co1–O3 2.035(2), Co1–O6 2.025(2).

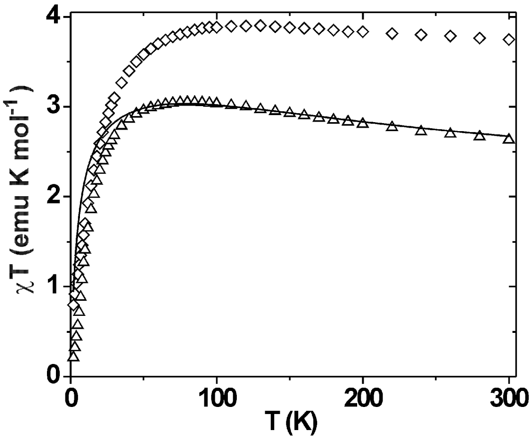


Fig. 2 χT *vs.* T plots for **3** (△) and **4** (◇). The solid line corresponds to the data fit using the parameters described in the text.

parameters: $2J_{\text{Ni–vd}} = +188\ \text{cm}^{-1}$, $2J_{\text{vd–vd}} = -42\ \text{cm}^{-1}$, TIP = 0.0001 $\text{cm}^3\ \text{mol}^{-1}$, = 0.005, = −3 K. The simulation does not give a very good fit at low temperatures with the given Weiss constant (R = 0.212 for all data, where $R = [([\Sigma(\chi_{\text{obs}}T - \chi_{\text{calc}}T)^2/\chi_{\text{obs}}T)^2]^{1/2})$. Larger Weiss constants (~ −15 to −20 K) improve the low-temperature data fit, but there are no close intermolecular contacts in the crystal packing of this molecule to justify such a large value. We therefore believe the rapid decrease in χT at low temperatures to arise from a *combination* of moderate intermolecular antiferromagnetic exchange and zero-field splitting. Unfortunately quantitative modelling incoporating both parameters is impractical because of the large number of interdependent parameters. However, the high temperature (> 80 K) data fit is very good (R = 0.0036 for data above 80 K). The ferromagnetic exchange between Ni(II) and coordinated verdazyls is consistent with our previous studies on related nickel–verdazyl complexes.[9–11] The intramolecular antiferromagnetic exchange between the two coordinated radicals likely arises from the fact that the two radicals are coplanar in the *xy* (equatorial) plane of the metal, thereby permitting superexchange *via* one of the nickel t_{2g} orbitals. This behaviour has been observed in metal–nitroxide complexes with similar geometric arrangement of radicals about a metal.[12,13]

The room temperature value of χT for the Co complex **4** (3.75 emu K mol^{-1}) is also significantly higher than the expected spin-only value (2.625 emu K mol^{-1}) for uncorrelated spins resulting from one high-spin cobalt(II) ion and two verdazyl radicals. As the temperature is decreased, χT gradually increases to a maximum value of 3.90 emu K mol^{-1} at about 130 K, and then rapidly decreases below 20 K. The low temperature behaviour likely arises from a combination of intermolecular exchange, zero-field splitting, and spin–orbit effects. The profile of the high-temperature data suggests that moderate intramolecular Co–verdazyl ferromagnetic interactions are present. However, quantitative modelling of magnetic data for octahedral cobalt(II) complexes engaged in exchange interactions with coordinated radicals is well-known to be problematic, pirimarily because of the strong spin–orbit coupling arising from the $^4T_{1g}$ ground electronic state.[14–19] This leads to significant orbital contributions to the magnetic moment and also induce large anisotropy components in the spin Hamiltonian. Further experiments are required[20] to fully understand the nature of the exchange interactions in this verdazyl–cobalt system. However, modelling of the high-temperature data using a simple isotropic Hamiltonian ($\boldsymbol{H} = -2J_{\text{Co–vd}}(\boldsymbol{S}_{\text{vd1}}\boldsymbol{S}_{\text{Co}} + \boldsymbol{S}_{\text{vd2}}\boldsymbol{S}_{\text{Co}}) - 2J_{\text{vd–vd}}\boldsymbol{S}_{\text{vd1}}\boldsymbol{S}_{\text{vd2}}$, where $\boldsymbol{S}_{\text{Co}}$ = 3/2 and $\boldsymbol{S}_{\text{vd1}} = \boldsymbol{S}_{\text{vd2}} = ½$) and setting g_{vd} = 2 and g_{Co} = 2.4 produced the following parameters as an estimate of the exhange parameters: $2J_{\text{Co–vd}} = +68\ \text{cm}^{-1}$, $2J'_{\text{vd–vd}} = -38\ \text{cm}^{-1}$. These are comparable in magntiude to related Co complexes containing two coordinated imino nitroxides.[19]

In summary, we have prepared a simple verdazyl radical derivative exhibiting high solubility in water and demonstrated its utility as a chelating ligand. This opens up new avenues for the preparation of metal–radical assemblies, for example using hydrothermal techniques, and potentially creating polymeric networks with novel magnetic properties consisting of the verdazyl-carboxylate ligand coordinating in a *bis*-bidentate mode.

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Notes and references

† *Synthesis* of Ni complex **3**: $NiCl_2{\cdot}6H_2O$ (145 mg, 0.61 mmol) was added to a solution of **1** (204 mg, 1.17 mmol) in distilled water (10 mL) and the mixture was stirred until all of the solid had dissolved. Aqueous NaOH (2 M) was then added to the mixture (0.58 mL, 1.16 mmol) and the solution immediately turned pale yellow with a voluminous grey precipitate that settled to the bottom of the flask. The mixture was left undisturbed and open to the atmosphere at room temperature for 96 h, during which time well-formed dark red crystals formed which were filtered off and washed with cold distilled water, yield 70 mg (24%). Anal. Calc. for $C_{10}H_{16}N_8O_8$-$Ni{\cdot}2H_2O$: C, 25.49; H, 4.28; N, 23.78. Found: C, 25.74; H, 3.75; N, 24.12%. $\lambda_{\max}$/nm (ε/M^{-1} cm^{-1}) (DMSO): 399 (4.9 × 10^3), 452 (1.6 × 10^3). The corresponding Co complex **4** was prepared analogously, yield 52%. Anal. Calc. for $C_{10}H_{16}N_8O_8Co{\cdot}2H_2O$: C, 25.50; H, 4.28; N, 23.79. Found: C, 25.83; H, 3.71; N, 23.81%.

‡ *Crystal data* for **3**: $C_{10}H_{20}N_8NiO_{10}$, M = 471.05, triclinic, space group $P\bar{1}$, a = 9.1957(18), b = 9.4812(19), c = 10.539(2), α = 85.450(3), β = 84.058 (3), γ = 79.127(3), V = 895.8(3) Å^3, T = 293 K, Z = 2, λ(Mo-Kα) = 1.16 mm^{-1}, 6814 reflections measured, 3146 unique, R_1 = 0.036, wR_2 = 0.101, GOF = 1.07.

For **3**: $C_{10}H_{20}N_8CoO_{10}$, M = 471.27, triclinic, space group $P\bar{1}$, a = 9.1698(16), b = 9.6053(17), c = 10.5113(18), α = 84.802(3), β = 83.613(3), γ = 79.995(3), V = 903.7(3) Å^3, T = 293 K, Z = 2, λ(Mo-Kα) = 1.02 mm^{-1}, 6874 reflections measured, 3168 unique, R_1 = 0.031, wR_2 = 0.091, GOF = 1.011. CCDC reference numbers 186282 and 186283. See http://www.rsc.org/suppdata/cc/b2/b204851e/ for crystallographic data in CIF or other electronic format.

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