DALTON
FULL PAPER

Synthesis and structure of di-μ-bromo-bis[(1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl)copper(I)] †

David J. R. Brook,*[a] Spring Fornell,[a] Bruce Noll,[b] Gordon T. Yee[b] and Tad H. Koch[b]

[a] *Department of Chemistry and Biochemistry, University of Detroit Mercy, 4001 W. Mc.Nichols Rd., Detroit, Michigan 48221, USA*
[b] *Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, CO 80309-0215, USA*

Received 27th October 1999, Accepted 24th April 2000
Published on the Web 9th June 2000

Reaction of the verdazyl precursor 1,4,5,6-tetrahydro-2,4-dimethyl-6-(2′-pyridyl)-1,2,4,5-tetrazin-3(2*H*)-one (pvdH$_3$) with oxygen and copper(I) bromide in acetonitrile results in precipitation of the crystalline diradical di-μ-bromo-bis[(1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl)copper(I)]. The solid shows a slightly anisotropic ESR spectrum and magnetic susceptibility measurements indicate weak antiferromagnetic exchange between the free radicals, consistent with the assignment as a copper(I) ion coordinated to a free radical.

Introduction

Interest in radical ligands is growing as a result of a more general interest in molecule-based magnetism. Unpaired electrons on the ligand of a coordination compound can allow stronger interaction between magnetic metal ions,[1] while careful ligand design can lead to greater structural control, the overall goal being to design materials with specific magnetic properties. The biggest problem with this approach is the synthesis of stable organic radicals that can also serve as ligands. Many of the currently studied free radical ligands, including semiquinones, nitroxides and nitronyl nitroxides, coordinate through an oxygen atom.[1] As a result they are relatively hard bases and poor π acceptors. Because the ligand unpaired electron is typically in a π type orbital there is weak interaction between ligand and metal unpaired electrons. Stronger metal–radical interactions might be obtained with a species that has greater π acidity[2] and a large spin density on the coordinating atom. Examples include iminonitroxide radicals[3–6] and the radical anionic ligands TCNE,[7,8] DCNQI (dicyanobenzoquinone diimine)[9,10] and TCNQ,[11] the coordination compounds of which all show novel magnetic and electronic properties. The 6-oxoverdazyl radical, first described by Neugebauer and Fischer,[12a] is also a promising candidate for this role. Calculations and ESR spectroscopy indicate that the verdazyl unpaired electron is delocalized over the four nitrogen atoms.[12–15] Two of these have a lone pair available for metal coordination making the verdazyl ring system a bridging ligand analogous to pyrimidine. Furthermore, polyazine heterocycles are typically π electron deficient and thus relatively strong π acceptors allowing significant mixing of metal and ligand centered π orbitals.[16–18] Polyazine heterocyclic ligands have also been extensively utilized in the construction of complex coordination arrays and polymers.[19] Because of their geometry, chelating ability and paramagnetism verdazyl radicals may provide an important complement to polyazine ligands in the design and synthesis of nanoscale devices.

As a first step to understanding the properties of metal–verdazyl coordination polymers, we are seeking to characterize the extent of metal–ligand interaction in copper(I) verdazyl coordination compounds. Previous studies on copper(I) coordination compounds of the diradical ligand 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-bis(verdazyl) (bvd) revealed an unusually fast spin relaxation rate for the radicals.[20] Two possible mechanisms were proposed for this phenomenon. One of these involves interaction with the neighboring diradical along the polymer chain; and the other involves relaxation through interaction with a second low lying triplet state possibly with metal to ligand charge transfer (MLCT) character. Discrimination between the mechanisms was not possible based on the available data, since the only available solution species, which also showed fast spin relaxation, was only poorly characterized and possibly oligomeric. No other evidence was available to determine the energy, or even support the existence of the inferred MLCT state. The problems involved in characterizing these systems may be traced, in part, to the ready formation of stable coordination polymers with the bvd bridging ligand. The 3-(2-pyridyl)oxoverdazyl ligand, unlike bvd, contains only one chelating coordination site and is thus suited to form discrete systems. We report here our initial results with copper(I) coordination compounds of this free radical.

Experimental

General

1,4,5,6-Tetrahydro-2,4-dimethyl-6-(2-pyridyl)-1,2,4,5-tetrazin-3(2*H*)-one (pvdH$_3$) and 1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl (pvd) were synthesized as described elsewhere.[21] Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. IR spectra were measured by diffuse reflectance on samples dispersed in powdered potassium bromide using a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer. UV-vis spectra were recorded on a Hewlett-Packard HP-8452 diode array spectrophotometer. X-Band ESR spectra were recorded on a Bruker ESP-300E spectrometer equipped with a variable temperature controller. Magnetic susceptibilities were recorded on a Quantum Design MPMS-5 SQUID magnetometer.

Di-μ-bromo-bis[(1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl)-copper(I)], [CuBr(pvd)]$_2$

The ligand pvdH$_3$ (20.7 mg, 0.1 mmol) in acetonitrile (1 mL) and CuBr (15 mg, 0.1 mmol) in acetonitrile (1 mL) were

---

† The IUPAC name for oxoverdazyl is 3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl.

DOI: 10.1039/a908563g

combined in a screw cap vial. After standing 12 h, red-black crystals had formed and the O_2 within the vial was depleted. The supernatant solution was decanted into a second vial allowing further oxidation and a second crop of crystals grew. The combined yield of black, crystalline $[CuBr(pvd)]_2$ was 14 mg (40%) (Found: C, 31.17; H, 2.84; N, 19.97. $C_{18}H_{20}Br_2Cu_2N_{10}O_2$ requires C, 31.09; H, 2.90; N, 20.14%). IR (diffuse reflectance in KBr) ν_{max}/cm^{-1} 3092 (aromatic C–H), 2929 (methyl C–H), 1701 (C=O), 1653, 1591, 1476, 1293, 1257, 1148, 1096, 1022, 800, 752, 713, 669, 654, 547, 537 cm^{-1}. A single, needle shaped crystal with dimensions 0.36 × 0.06 × 0.06 mm was mounted in silicone grease for X-ray crystallography.

Crystal data

$C_{18}H_{20}Br_2Cu_2N_{10}O_2$, $M = 347.67$, monoclinic, $a = 6.9489(1)$, $b = 16.439$, $c = 10.4900(1)$ Å, $\beta = 99.23°$, $V = 1182.78(2)$ Å^3, $T = 161$ K, space group $P2_1/c$, (no. 14) $Z = 4$, μ(Mo-Kα) = 5.215 mm^{-1}, 10688 reflections were collected of which 3557 unique ($R_{int} = 0.032$). Solution (direct methods) and refinement gave a final $wR(F^2)$ of 0.0795 (all data).

CCDC reference number 186/1960.

See http://www.rsc.org/suppdata/dt/a9/a908563g/ for crystallographic files in .cif format.

Results

The immediate precursor to pvd, 1,4,5,6-tetrahydro-2,4-dimethyl-6-(2-pyridyl)-1,2,4,5-tetrazin-3(2*H*)-one (pvdH_3), was readily synthesized by condensation of dimethylcarbonohydrazide with pyridine-2-carboxaldehyde in methanol solvent as described elsewhere.[21] Oxidation of pvdH_3 with ferricyanide in water gives a product mixture containing the free radical pvd and ferrocyanide but we have not been able to purify the radical because of its slow decomposition.[21] Because of the problems associated with isolating pvd, we chose to attempt the formation of coordination compounds of pvdH_3 with the intent of subsequent oxidation. Combination of acetonitrile solutions of copper(I) bromide and pvdH_3, in air, produced over a period of 48 h a dark brown solution that deposited dark red-black crystals. Upon examination of the compound by single crystal X-ray diffraction, we were surprised to find that this was not the anticipated coordination compound of pvdH_3 but rather a compound of the free radical pvd: di-μ-bromo-bis[(1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl)copper(I)], $[CuBr(pvd)]_2$. A thermal ellipsoid plot of this structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The molecule is dimeric with two oxoverdazyl ligands linked by a copper halide bridge. The molecule is located on a center of symmetry. The copper halide bridge is slightly asymmetric with two Cu–Br distances of 2.406 Å and 2.493 Å. The copper–copper distance is short (2.558 Å) but this is unremarkable for copper(I) halide coordination compounds.[22] The oxoverdazyl ligand is planar, with bond lengths and angles similar to those measured for other oxoverdazyl free radicals.[13,20] ESR spectra of a polycrystalline sample of $[CuBr(pvd)]_2$ at room temperature showed a relatively featureless, strongly exchange narrowed signal with a linewidth of 5 G and g tensor components (obtained through simulation) $g_{xx} = 2.015$, $g_{yy} = 2.01$ $g_{zz} = 2.0058$. The temperature dependence of the ESR spectrum shows essentially Curie behavior from 120 to 300 K consistent with the magnetic data. Magnetic susceptibility measurements were recorded from 1.8 K to 300 K and the data are plotted in Fig. 2. At 300 K $[CuBr(pvd)]_2$ shows the expected susceptibility corresponding to two weakly interacting unpaired electrons per dimer. The plot of χT *vs.* T is almost temperature independent near 300 K but decreases sharply due to antiferromagnetic exchange at low temperatures. The best fit to the susceptibility data is obtained with a linear Heisenberg model[23] with an antiferromagnetic exchange constant of $J = -5$ cm^{-1}. This can be rationalized by inspection of the molecular packing. The radicals are arranged in chains connected through π-stacking interactions. Each verdazyl ring overlaps with the pyridine ring of the next radical in the chain with a distance of approximately 3.3 Å between the rings (Fig. 3). Copper halide bridges link the chain to alternate neighboring chains (Fig. 4). A similar arrangement was observed in the copper(I) halide bridged coordination compounds of pyridyliminonitroxide ligands.[4] Though the fit to the one-dimensional model above is good, the exchange energy must be treated with caution since the model ignores interchain interaction through halide bridges. A simple dimer model can also be used to fit the data giving an exchange interaction of $J/k = -17$ K but again, this ignores the π stacking interaction. Without low temperature ESR data on isolated molecules we cannot reliably distinguish between these models or assign an intermediate model. The compound is slightly soluble in acetonitrile; however, solution ESR spectra reveal only a single broad (30 G) signal with no resolved hyperfine coupling.

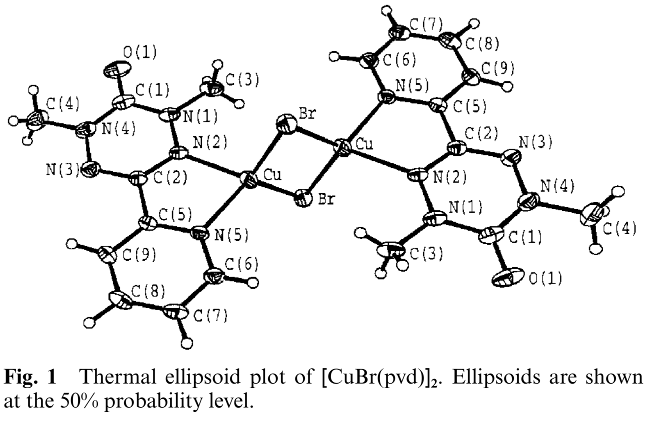

Fig. 1 Thermal ellipsoid plot of $[CuBr(pvd)]_2$. Ellipsoids are shown at the 50% probability level.

Table 1 Bond lengths (Å) and angles (°) for $[CuBr(pvd)]_2$

Cu–Cu(A)	2.5580(6)	N(2)–C(2)	1.334(3)
Cu–Br	2.4927(4)	C(2)–N(3)	1.326(3)
Cu–Br(A)	2.4060(4)	N(3)–N(4)	1.371(3)
Cu–N(2)	2.057(2)	N(4)–C(1)	1.376(4)
Cu–N(5)	2.052(2)	C(1)–O(1)	1.218(3)
N(1)–N(2)	1.368(3)	C(1)–N(1)	1.376(4)
Br–Cu–Br(A)	117.072(14)	N(1)–N(2)–C(2)	115.9(2)
N(2)–Cu–N(5)	79.27(8)	N(2)–C(2)–N(3)	127.2(2)
N(2)–Cu–Br	107.59(6)	C(2)–N(3)–N(4)	114.4(2)
N(2)–Cu–Br(A)	116.95(6)	N(3)–N(4)–C(1)	124.5(2)
N(5)–Cu–Br	110.28(6)	N(4)–C(1)–N(1)	115.1(2)
N(5)–Cu–Br(A)	119.50(6)	C(1)–N(1)–N(2)	122.9(2)

Discussion

The only other crystallographically characterized metal coordination compounds of verdazyl radicals are the copper(I) halide coordination compounds of the diradical bvd.[20] We have reported spectroscopic evidence for Zn, Cd, and Hg coordination compounds of pvd but pure samples could not be obtained.[21] Previous attempts to react metal halides with verdazyl radicals only resulted in oxidation of the radical by the metal center[24,25] or disproportionation.[26,27] Our characterization of $[CuBr(pvd)]_2$ and other metal-oxoverdazyl coordination compounds[20,21] points to the greater stability of the 6-oxoverdazyls in coordinating environments. Furthermore, coordination of copper(I) to pvd appears to result in stabilization of both the free radical (which has not yet been isolated) and the copper(I) oxidation state. An affinity for copper(I) over copper(II) was also demonstrated for the 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-bis(verdazyl) (bvd) ligand.[20] For bvd, experimental measurements,[20] supported by calculation,[28] indicate that significant overlap occurs between the half-occupied

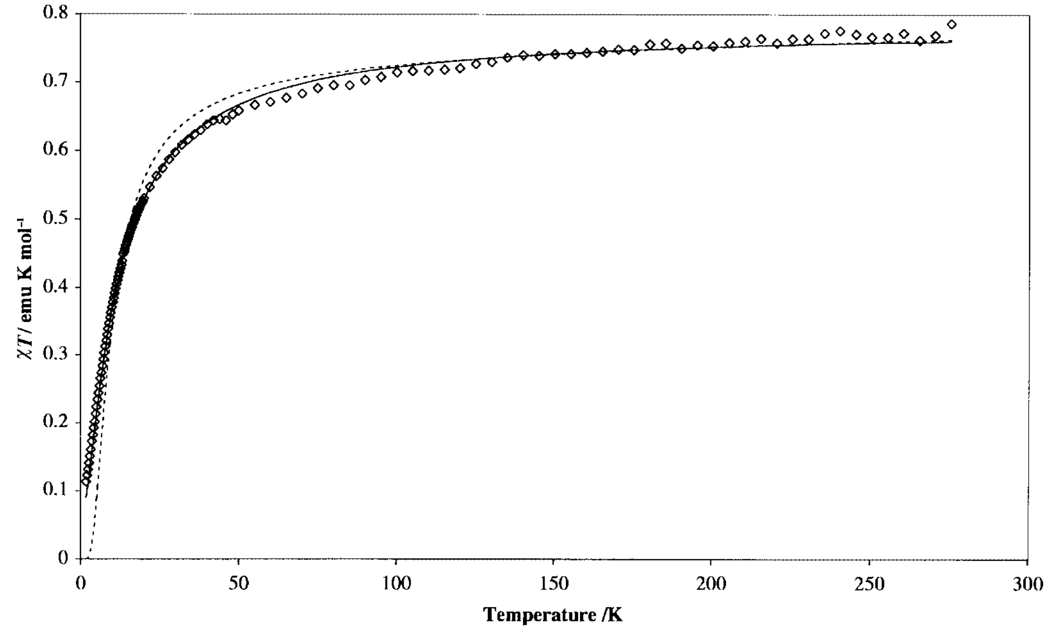

Fig. 2 Magnetic susceptibility data for $[CuBr(pvd)]_2$. The solid line is a best fit to the linear antiferromagnet model of Smith and Friedberg[25] while the dashed line is a best fit to the Bleaney–Bowers dimer model.

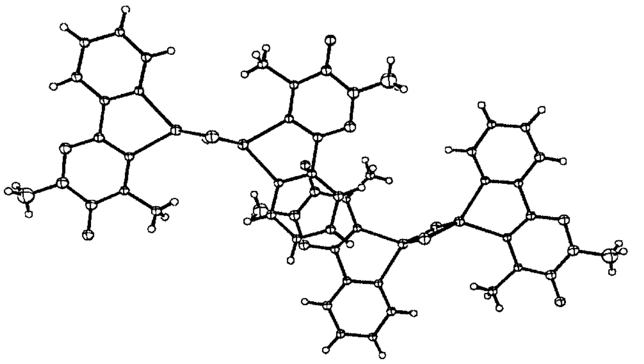

Fig. 3 Overlap between the verdazyl and pyridine rings in the structure of $[CuBr(pvd)]_2$.

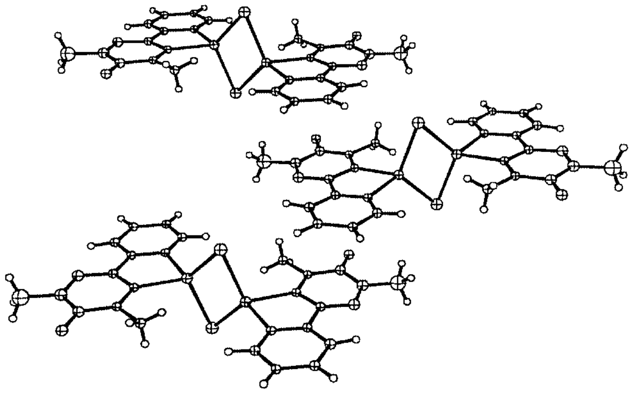

Fig. 4 Packing of molecules in $[CuBr(pvd)]_2$.

verdazyl orbital and the filled copper d orbitals resulting in delocalization of spin density onto copper. ESR data suggest a similar delocalization for $[CuBr(pvd)]_2$. The solid state ESR signal is narrow and slightly anisotropic supporting the assignment as a copper(I) coordination compound of an organic free radical with anisotropy arising from delocalization onto a copper d orbital. Unfortunately hyperfine coupling that would confirm the delocalization is masked by the dimeric nature of the molecule. The magnetic data indicate overall weak antiferromagnetic exchange but because of the crystal packing it is harder to ascribe this to delocalization onto copper. For the related iminonitroxide coordination compound of CuI, exchange between radicals across a halide bridge was estimated to be ≈2 cm^{-1},[4] though this determination was beset with the same problems in regard to crystal packing and the resolution of π-stacking *vs.* halide bridge interactions. The pvd coordination compound does not show unusually fast spin relaxation indicating that the relaxation observed with the $Cu_2X_2(bvd)$ polymers (X = halogen) is a phenomenon associated with the diradical ligand.

Conclusion

1,4,5,6-Tetrahydro-2,4-dimethyl-6-(2-pyridyl)-1,2,4,5-tetrazin-3(2*H*)-one ($pvdH_3$) is oxidized by air in the presence of copper(I) bromide in acetonitrile to give the diradical di-μ-bromo-bis[(1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl)-copper(I)]. The strong driving force to form copper(I) compounds of the radical ligand supports the idea of a significant metal–ligand π interaction; however, ESR has been unable to detect hyperfine interactions with the copper nucleus. We assume this is a result of rapid exchange between radical centers. 6-Oxoverdazyl ligands, as both stable, neutral free radicals, and polyazine ligands with significant π acceptor character, show considerable potential as building blocks for functional metal–organic assemblies.

Acknowledgements

Funding was provided by the Petroleum Research Fund (31622-AC to T. H. K.) and the University of Detroit Mercy Faculty Grant Incentive Program (to D. J. R. B.). Crystallographic data was collected on instrumentation acquired under National Science Foundation Grant CHE-9505926.

References

1 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.
2 W. R. Entley and G. S. Girolami, *Science*, 1995, **268**, 397.
3 H. Oshio, T. Watanabe, A. Ohto, T. Ito and U. Nagashima, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 670.
4 H. Oshio, T. Watanabe, A. Ohto, T. Ito and H. Masuda, *Inorg. Chem.*, 1996, **35**, 472.
5 H. Oshio, U. Makato, T. Fukushi and T. Ito, *Chem. Lett.*, 1997, 1065.

6 H. Oshio, T. Watanabe, A. Ohto and T. Ito, *Inorg. Chem.*, 1997, **36**, 1608.

7 J. S. Miller and A. J. Epstein, *Chem. Commun.*, 1998, 1319.

8 J. S. Miller, J. C. Calabrese, R. S. McLean and A. J. Epstein, *Adv. Mater.*, 1992, **4**, 498.

9 S. Hunig, M. Kemmer, H. Meixner and H. C. Wolf, *Eur. J. Inorg. Chem.*, 1999, **5**, 899.

10 S. Hunig, *J. Mater. Chem.*, 1995, **5**, 1469.

11 K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1659.

12 (*a*) F. A. Neugebauer and H. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1980, **92**, 761; (*b*) S.-I. Nagaoka, K. Mukai and U. Nagashima, *J. Mol. Struct.* (*THEOCHEM*), 1998, **455**, 199.

13 D. J. R. Brook, H. H. Fox, V. Lynch and M. A. Fox, *J. Phys. Chem.*, 1996, 2066.

14 F. A. Neugebauer, H. Fischer and C. Kreiger, *J. Chem. Soc., Perkin Trans. 2*, 1993, 535.

15 F. A. Neugebauer, H. Fischer and R. Siegel, *Chem. Ber.*, 1988, **121**, 815.

16 W. Kaim and J. Fees, *Z. Naturforsch., Teil B*, 1995, **50**, 123.

17 A. Klein, S. Hasenzahl and W. Kaim, *Organometallics*, 1998, **17**, 3532.

18 M. Ketterle, J. Fiedler and W. Kaim, *Chem. Commun.*, 1998, 1701.

19 J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.

20 D. J. R. Brook, B. Conklin, V. Lynch and M. A. Fox, *J. Am. Chem. Soc.*, 1997, **119**, 5155.

21 D. J. R. Brook, S. Fornell, J. E. Stevens, B. Noll, T. H. Koch and W. Eisfeld, *Inorg. Chem.*, 2000, **39**, 562. See also C. L. Barr, P. A. Chase, R. G. Hicks, M. T. Lemaire and C. L. Stevens, *J. Org. Chem.*, 1999, **64**, 8893.

22 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988.

23 T. Smith and J. Friedberg, *Phys. Rev.*, 1968, **176**, 660.

24 G. F. Dvorko and L. S. Degtyarev, *Zh. Org. Khim.*, 1974, **10**, 1554.

25 G. F. Dvorko, L. S. Degtyarev and A. K. Tomaschik, *Dokl. Acad. Nauk SSSR*, 1972, **202**, 1073.

26 L. S. Degtyarev, Y. A. Maletin and A. A. Stetsenko, *Zh. Obshch. Khim.*, 1981, **51**, 2387.

27 N. G. Strizhakova, Y. A. Maletin and I. A. Sheka, *Zh. Obshch. Khim.*, 1983, **53**, 498.

28 M. T. Green and T. A. McCormick, *Inorg. Chem.*, 1999, **38**, 3061.