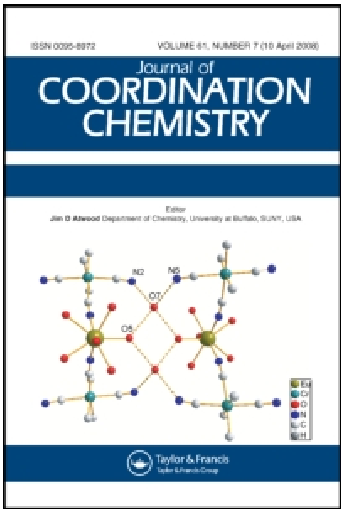

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Synthesis, structural, and magnetic properties of a supramolecular assembly constructed from radical cations and $[Au(CN)_2]^-$ anions

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Synthesis, structural, and magnetic properties of a supramolecular assembly constructed from radical cations and $[Au(CN)_2]^-$ anions

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A supramolecular assembly of $[p\text{-MePyNN}]_2[Au(CN)_2]_2$ (**1**) ($p\text{-MePyNN}^+ = $ 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazo-1-oxyl-3-oxide radical cation) has been synthesized from the combination of *p*-*N*-methylpyridinium nitronyl nitroxide radical cations and $[Au(CN)_2]^-$ anions, and characterized structurally as well as magnetically. The compound crystallizes in the orthorhombic, space group $P2_12_12_1$, with two independent $p\text{-MePyNN}^+$ cations separated from each other by the dimer $[Au(CN)_2^-]_2$. The magnetic study shows that the larger steric hindrance of $[Au(CN)_2]^-$ anion influences the magnetic interactions between the radical cations, with very weak antiferromagnetic interactions.

Keywords: Supramolecular complex; Nitronyl nitroxide radical; Crystal structure; Magnetism

1. Introduction

Radical cation of *N*-methylpyridinium nitronyl nitroxide ($MePyNN^+$) is a stable organic radical, which can have magnetic interactions between themselves or with other open-shell entities in radical salt compounds [1, 2]. In supramolecular assemblies of radical cations with other anions, open shell anions will have magnetic interactions with radical cations in the absence of chemical bonds through space, and even the close shell anions will also influence the magnetic interactions between the adjacent radical cations in the system. Such compounds are good examples for the study of magnetic interactions through space [3–15].

Many open-shell anions have been utilized in such radical salt compounds. Awaga *et al*. [7, 10] reported radical salts of $[MCl_4]^{2-}$ [M = Mn(II) and Co(II)] as the anions, and explained the nature of the M-Cl-*p*-rad$^+$ interactions based on a charge transfer mechanism from the 3*d* orbitals of the metal to the spin occupied molecular orbital of the nitronyl nitroxide cation; Kahn *et al*. [3, 11, 12] also reported radical cationic

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salts with $[Fe(CN)_6]^{3-}$ and $Mn_2\,[Cu(opba)]_3^{2-}$ [opba = *O*-phenylenebis(oxamato)] which shows 3-D magnetic interactions. Some small closed shell anions like I^- and ClO_4^- were also introduced to the field of radical salt compounds, and their existence influences the packing modes of the radicals and makes them usually have antiferromagnetic interactions [13]. The influence of closed shell anions with bigger steric hindrance on magnetic interactions between radicals has been less studied [14, 15]. $[Au(CN)_2]^-$ anions with aurophilic interactions usually have larger steric hindrance compared with other anions [16]. In this article we design a radical salt compound with $[Au(CN)_2]^-$ as the anion and reported the syntheses, structure, and magnetic properties of $[p\text{-MePyNN}]_2[Au(CN)_2]_2$.

2. Experimental

2.1. *Materials and methods*

All starting materials were of analytical grade and used without purification. The cationic free radical (*p*-MePyNNI = [4-(4,4,5,5-tetramethyl-1-oxido-3-oxyl-4,5-dihydro-3*H*-imidazol-2′-yl)-1-methylpyridinium] iodide) was prepared according to the literature procedure [2, 13, 17–20].

Elemental analyses for C, H, and N were carried out on a Perkin–Elmer elemental analyzer (model 240). Infrared spectra were obtained on a Bruker Tensor 27 Fourier transform infrared spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. Variable temperature magnetic susceptibility was measured on a SQUID magnetometer in a magnetic field of 5000 Oe (between 2 and 300 K). The molar magnetic susceptibility was corrected from the sample holder and diamagnetic contributions of all constituent atoms by using Pascal's constants [21].

2.2. *Preparation of (p-rad)$_2$[Au(CN)$_2$]$_2$ (1)*

p-MePyNNI (37.7 mg, 0.1 mmol) was dissolved in water (20 mL) and $KAu(CN)_2$ was added (29.8 mg, 0.1 mmol) under stirring at room temperature. After stirring for 2 h, the resulting small quantity of precipitate was filtered off, and then green crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate at room temperature. Yield 65%. Calcd for $C_{30}H_{38}Au_2N_{10}O_4$ (%): C, 36.15; H, 3.84; N, 14.05; Found (%): C, 36.10; H, 3.69; N, 13.95. IR (KBr disc, cm^{-1}) 2137 ($\nu_{(C\equiv N)}$), 1637 ($\nu_{s(C\cdots N)}$), and 1375 cm^{-1} ($\nu_{(NO)}$).

2.3. *X-ray structure determination*

X-ray diffractions were measured on an APEX II CCD area detector equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of crystallographic data is given in table 1. Empirical absorption corrections by semi-empirical from equivalents were carried out. The structure was solved by direct methods using SHELXS-97 and refined with SHELXL-97 [22, 23] by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, while hydrogens were located

Table 1. Summary of crystallographic data for **1**.

Empirical formula	$C_{30}H_{38}Au_2N_{10}O_4$
Formula weight	996.64
Temperature (K)	113(2)
Wavelength (Å)	0.71070
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	
a	12.5280(5)
b	12.7210(5)
c	21.5713(10)
Volume (Å^3), Z	3437.8(2), 4
Calculated density (mg m^{-3})	1.926
Absorption coefficient (mm^{-1})	8.575
$F(000)$	1912
Crystal size (mm^3)	0.20 × 0.18 × 0.10
θ range for data collection (°)	1.86–27.88
Limiting indices	$-16 \le h \le 16$; $-16 \le k \le 16$; $-28 \le l \le 28$
Reflections collected/unique	32523/8145 [$R_{int} = 0.0556$]
Completeness to $\theta = 27.88$ (%)	99.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4810 and 0.2789
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8145/6/427
Goodness-of-fit on F^2	0.970
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0539$
R indices (all data)	$R_1 = 0.0361$, $wR_2 = 0.0556$
Absolute structure parameter	−0.010(7)
Largest difference peak and hole (e Å^{-3})	1.176 and −1.675

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths			
Au(1)–C(2)	2.012(6)	O(1)–N(6)	1.283(5)
Au(1)–C(1)	2.022(6)	O(2)–N(7)	1.286(5)
Au(1)–Au(2)	3.3017(3)	O(3)–N(9)	1.270(5)
Au(2)–C(3)	1.996(6)	O(4)–N(10)	1.290(5)
Au(2)–C(4)	2.028(6)		
Bond angles			
C(2)–Au(1)–C(1)	175.74(19)	C(3)–Au(2)–C(4)	175.6(2)
C(2)–Au(1)–Au(2)	78.27(13)	C(3)–Au(2)–Au(1)	84.83(16)
C(1)–Au(1)–Au(2)	105.93(13)	C(4)–Au(2)–Au(1)	99.51(17)

geometrically and refined isotropically. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structure*

The compound crystallizes in the orthorhombic, space group $P2_12_12_1$, with $a = 12.5280(5)$ Å, $b = 12.7210(5)$ Å, $c = 21.5713(10)$ Å. As shown in figure 1, [p-MePyNN]$_2$ [Au(CN)$_2$]$_2$ consists of two p-MePyNN$^+$ cationic radicals separated from each other by

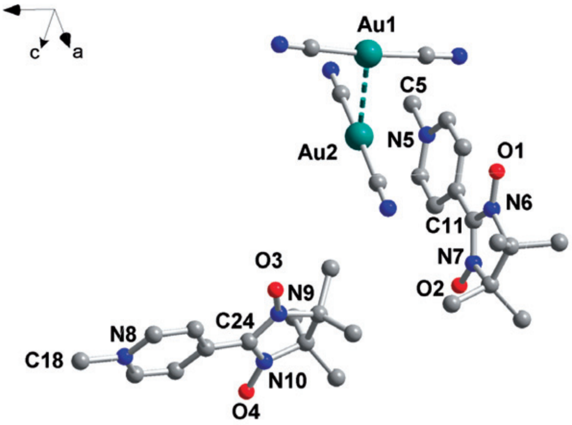

Figure 1. The molecular structure of **1**.

$[Au(CN)_2^-]_2$ (in which there are aurophilic interactions with Au···Au distance of 3.30 Å, and the two $[Au(CN)_2]^-$ are almost vertical to each other to make a bigger steric hindrance). The two *p*-MePyNN$^+$ radicals are discrete and not symmetrical in the relatively vertical position. The N–O bond distances are in the range of 1.27–1.29 Å, which are in good agreement with the previously reported ones [2, 6, 24]. In one radical, the pyridyl ring with N8 makes a dihedral angle of 13.29° with the mean plane of the O(3)–N(9)–C(24)–N(10)–O(4) π system containing the unpaired electron, while the pyridyl ring including N5 in the other radical makes a dihedral angle of 6.84° with the plane O(1)–N(6)–C(11)–N(7)–O(2), small compared with those in reported nitronyl nitroxide radicals and showing delocalization of π electron.

In the packing diagram for **1** (figure 2a), we can clearly see the packing mode of *p*-MePyNN$^+$ radicals and the big steric hindrance of $[Au(CN)_2^-]_2$. The N–O of adjacent *p*-MePyNN$^+$ radicals are separated by the big dimmer, $[Au(CN)_2^-]_2$, with a minimum intermolecular O···O distance of 5.88 Å (figure 2b). This situation is special in the context of magnetic materials containing *p*-MePyNN$^+$ with other small closed shell anions such as I^- or ClO_4^-, where shorter O···O contacts between adjacent radicals of about 3.16 Å are generally observed [13]. Figure 2(c) shows that the shortest intermolecular contact in two adjacent radicals involves O3 of N–O from one radical and the sp^2 carbon C6 from another, with O3···C6 = 3.18 Å.

3.2. *Magnetic properties*

Magnetic properties of **1** in the form of $\chi_M/\chi_M T$ *versus* T (where χ_M is the magnetic susceptibility for half a $[p\text{-MePyNN}]_2[Au(CN)_2]_2$ unit) are presented in figure 3. At room temperature, the $\chi_M T$ is 0.375 cm^3 mol^{-1} K, consistent with the value (0.375 cm^3 mol^{-1} K) expected for an uncoupled system with one *p*-MePyNN$^+$ ($S = 1/2$). Upon cooling, the $\chi_M T$ value has almost no change till 30 K, where it begins to decrease sharply to 0.28 cm^3 mol^{-1} K at 2 K. For this kind of system which has only one kind of interaction between radical cations through space and the χ_M value does not show a maximum even at low temperature, we simply studied the magnetic property by the

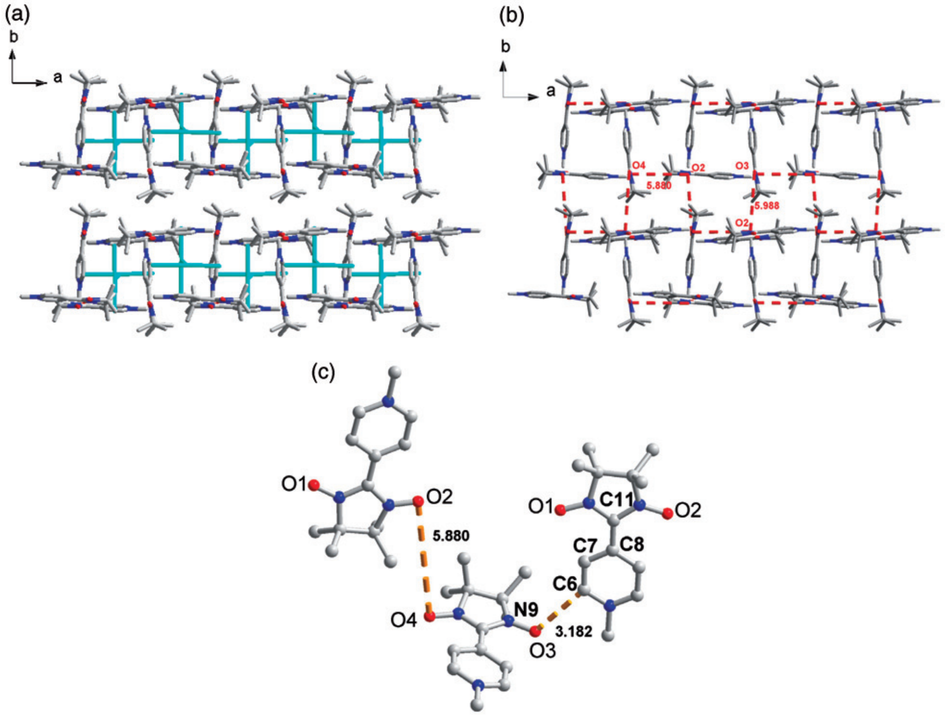

Figure 2. Packing diagram for **1**. (a) with $[Au(CN)_2^-]_2$. (b) omitting $[Au(CN)_2^-]_2$ and showing the shortest NO contact. (c) The shortest intermolecular contact in two adjacent radical between O3 and C6.

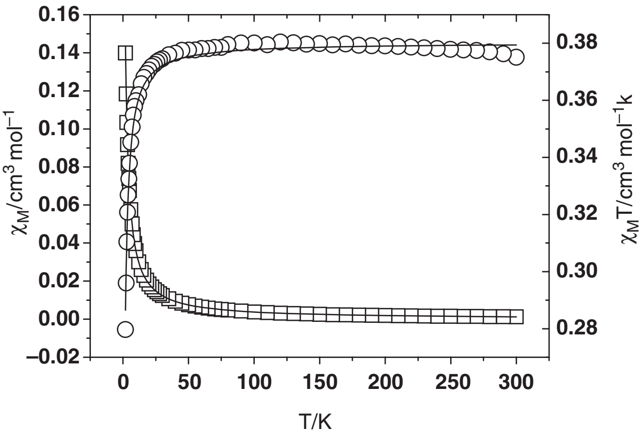

Figure 3. Plots of χ_M and $\chi_M T$ *vs.* T for **1**.

Curie–Weiss expression $\chi_M = Ng^2\beta^2S(S+1)/3K(T-\theta)$ in the range of 2–300 K, getting a negative Weiss constant of $\theta = -0.65$ K and $g = 2.01$, $R = 2.1 \times 10^{-4}$ (R value is defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$). Based on $\theta = 2zj'S(S+1)/3K$ [1], we obtained $zj' = -0.90\,\text{cm}^{-1}$, confirming a weak antiferromagnetic interaction between adjacent *p*-$MePyNN^+$ radicals, similar to those in magnetic materials containing *p*-$MePyNN^+$ radicals separated by anions like I^- and ClO_4^- [13]; the interactions between close radical cations are also antiferromagnetic.

The sign and magnitude of the intermolecular magnetic interactions usually depend strongly on the relative arrangement of the stacked radicals [25–27]. Structural analysis reveals that the shortest intermolecular contact in two adjacent radicals involves the oxygen of the N–O group from one radical and the sp^2 carbon atom from another, with $O3 \cdots C6 = 3.18$ Å (as shown in figure 2c). In *p*-MePyNN, assuming the positive spins populated over the N–O groups, spin polarization induces a small positive spin density on the sp^2 carbon C6. Based on McConnell's mechanism [28] that if molecules overlap with opposite signs of the spin density, an intermolecular ferromagnetic interaction would be expected, while overlap with same signs of the spin density results in antiferromagnetic interaction. The nearest two atoms O3 and C6, which carry the same sign of spin, result in weak antiferromagnetic interactions between adjacent radicals.

3.3. *Electron paramagnetic resonance spectrum*

The powder electron paramagnetic resonance (EPR) spectrum of **1** measured at room temperature with the medium wave frequency of 9.8580 GHz (figure 4) displays a slightly asymmetric absorption. From the above magnetic data, the very weak antiferromagnetic interactions between adjacent radicals with ground state $S = 0$ should have no EPR signal and so the asymmetric EPR absorption at room temperature should be due to population of the excited state of $S = 1$. The simulated spectrum (assuming $S = 1$) was then obtained with the parameters: $g_{\perp} = 2.0045$, $g_{||} = 2.0113$. The average g value 2.0068 agrees well with that obtained form the magnetic data $g = 2.01$.

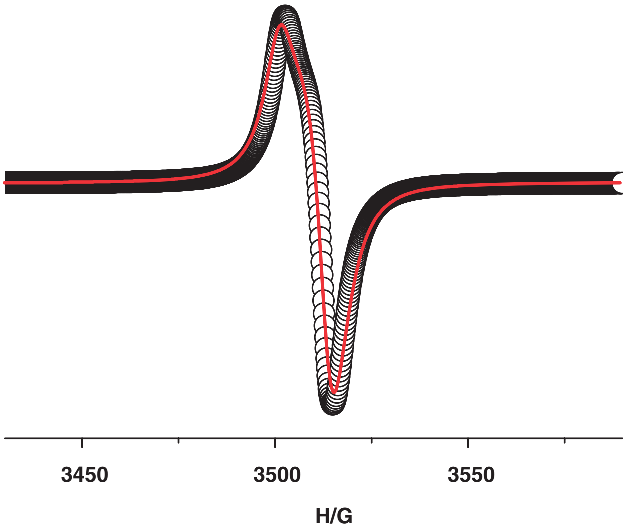

Figure 4. The powder EPR spectra for **1** at room temperature (line is simulated, circle is experiment data).

4. Conclusions

A new complex, formulated as $[p\text{-MePyNN}]_2[\text{Au(CN)}_2]_2$, characterized structurally and magnetically consists of two p-MePyNN$^+$ cations separated by the dimer $[\text{Au(CN)}_2^-]_2$. Magnetic study showed weak antiferromagnetic interactions between adjacent p-MePyNN$^+$ radicals through space separated by $[\text{Au(CN)}_2]^-$.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 671404 for **1**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] O. Kahn. *Molecular Magnetism*, VCH, New York (1993).

[2] A. Yamaguchi, K. Awaga, T. Inabe, T. Nakamura, M. Masumoto, Y. Maruyama. *Chem. Lett.*, **20**, 1777 (1991).

[3] C. Michault, L. Ouahab, P. Bergerat, O. Kahn, A. Bousseskou. *J. Am. Chem. Soc.*, **118**, 3610 (1996).

[4] R. Lescouezec, G. Marinescu, M. Munoz, D. Luneau, M. Andruh, F. Lloret, J. Faus, M. Julve, J. Mata, R. Llusar, J. Cano. *New J. Chem.*, **25**, 1224 (2001).

[5] G. Ballester, E. Coronado, J. Galan-Mascaros, C. Gimenz-Saiz, A. Nuez, F. Romero. *Polyhedron*, **20**, 1659 (2001).

[6] G. Ballester, E. Coronado, C. Giménz-Saiz, F. Romero. *Angew. Chem. Int. Ed.*, **40**, 792 (2001).

[7] H. Oshio, T. Yaginiuma, T. Ito. *Bull. Chem. Soc. Jpn.*, **73**, 1365 (2000).

[8] A. Alberola, E. Coronado, C. Giménez-Saiz, C.J. Gómez-García, F.M. Romero, A. Tarazän. *Eur. J. Inorg. Chem.*, 389 (2005).

[9] R. González, F. Romero, D. Luneau, D. Armentano, G.D. Munno, C. Kremer, F. Lloret, M. Julve, J. Faus. *Inorg. Chim. Acta*, **358**, 3995 (2005).

[10] Y. Yamaguchi, T. Okuno, K. Awaga. *Bull. Chem. Soc. Jpn.*, **69**, 875 (1996).

[11] H.O. Stumph, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn. *Science*, **261**, 447 (1993).

[12] H.O. Stumph, L. Ouahab, Y. Pei, P. Bergerat, O. Kahn. *J. Am. Chem. Soc.*, **116**, 3386 (1994).

[13] A. Yamaguchi, K. Awaga, T. Inabe, T. Nakamura, M. Masumoto, Y. Maruyama. *Chem. Lett.*, **22**, 1443 (1993).

[14] A. Tarazon, C. Gimenez-Saiz, C.J. Gomez-Gacia, F.M. Romero. *Molecules*, **9**, 782 (2004).

[15] T. Okuno, K. Kuwamoto, W. Fujita, K. Awaga, W. Nakanishi. *Polyhedron*, **22**, 2311 (2003).

[16] G.F. Xu, Z.Q. Liu, H.B. Zhou, Y. Guo, D.Z. Liao. *Aust. J. Chem.*, **59**, 640 (2006).

[17] K. Awaga, A. Yamaguchi, T. Okuno, T. Inabe, T. Nakamura, M. Matsumoto, Y. Maruyama. *J. Mater. Chem.*, **4**, 1377 (1994).

[18] K. Awaga, T. Okuno, A. Yamaguchi, M. Hasegawa, T. Inabe, Y. Maruyama, N. Wada. *Phys. Rev. B*, **49**, 3975 (1994).

[19] I. Hawkins, A.E. Underhill. *J. Chem. Soc., Chem. Commun*., 1593 (1990).

[20] O.A. Dyachenko, S.V. Konovalikhin, A.I. Kotov, G.V. Shilov, E.B. Yagubski, C. Faulmann, P. Cassoux. *J. Chem. Soc., Chem. Commun*., 508 (1993).

[21] P.W. Selwood. *Magnetochemistry*, p. 78, Interscience, New York (1956).

[22] G.M. Sheldrick. *SHELXS-97, Program for the Solution of Crystal Structures*, University of Gottingen, Germany (1997).

[23] G.M. Sheldrick. *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Gottingen, Germany (1997).

[24] K. Awaga, N. Wada. In *Magnetism: A Supramolecular Function*, NATO ASI Ser., Ser. C, O. Kahn (Ed.), Vol. 484, pp. 205–218, Kluwer, Dordrecht (1996).

[25] A. Caneschi, F. Ferrara, D. Gatteschi, P. Rey, R. Sessoli. *Inorg. Chem*., **29**, 1756 (1990).

[26] F.L. Panthou, D. Luneau, J. Laugier, P. Rey. *J. Am. Chem. Soc*., **115**, 9095 (1993).

[27] H. Oshio, T. Ito. *Coord. Chem. Rev*., **198**, 329 (2000).

[28] H.M. McConnell. *J. Chem. Phys*., **39**, 1910 (1963).