Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 7–9

Mendeleev Communications

Isolation of the 2,1,3-benzothiadiazolidyl radical anion: X-ray structure and properties of a [K(THF)][$C_6H_4N_2S$] salt

Sergey N. Konchenko,*[a] Nina P. Gritsan,*[b,c] Anton V. Lonchakov,[b,c] Udo Radius[d] and Andrey V. Zibarev*[c,e]

[a] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 383 330 9489; e-mail: konch@che.nsk.su*
[b] *Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 383 330 7350; e-mail: gritsan@kinetics.nsc.ru*
[c] *Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[d] *Institute for Inorganic Chemistry, University of Karlsruhe, 76131 Karlsruhe, Germany*
[e] *N. N. Vorozhtsov Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 383 330 9752; e-mail: zibarev@nioch.nsc.ru*

DOI: 10.1016/j.mencom.2009.01.003

The 2,1,3-benzothiadiazolidyl radical anion 1 was isolated for the first time in the form of the thermally stable salt [K(THF)][1], which was structurally characterized by X-ray diffraction.

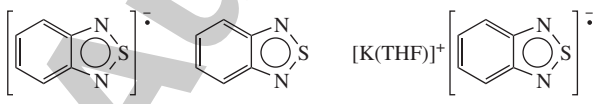
Spin-carrying chalcogen–nitrogen π-heterocycles belong to the most promising building blocks in the design and synthesis of magnetic and conducting molecular materials.[1–7] While neutral radicals and radical cations have been a subject of extensive studies, radical anions have been less studied.[1–7]

Recently, it has been found that chalcogen–nitrogen π-radical anions, in particular [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazolidyl, form thermally stable salts with various cations. Magnetic measurements on the salts revealed antiferromagnetic ordering of their spin systems at cryogenic temperatures.[7] These results motivate further research in the field focused, particularly, on new heterocyclic precursors and their radical anions. Another reason of interest is the general significance of π-radical anions for organic chemistry and its applications including materials science.[8]

The recognized precursors of persistent heterocyclic π-radical anions are 2,1,3-benzochalcogenadiazoles (chalcogen: S, Se, Te).[9] For the S and Se derivatives, the radical anions have been known since the 1960s from ESR experiments, but they have never been isolated in the form of the salts.[8,10]

This work reports on first isolation of 2,1,3-benzothiadiazolidyl radical anion (**1**, Scheme 1). To obtain **1**, 2,1,3-benzothiadiazole (**2**, Scheme 1) was treated with elemental potassium in THF as a solvent. The reaction solution revealed an ESR spectrum, which was in full agreement with that reported for **1** previously.[10] The experimental hfc constants ($a_N = 5.30$, $a_H = 2.65$, $a_H = 1.65$ G) are fairly well-reproduced by the DFT/UB3LYP/6-31G(d) calculations ($a_N = 5.35$, $a_H = 3.90$, $a_H = 1.50$). Further workup of the solution gave crystalline [K(THF)][**1**] (**3**, Scheme 1).[†] The salt is thermally stable but extremely sensitive towards atmosphere.

The structure of **3** was confirmed by XRD.[‡] In the solid state, each N and S atom of **1**, as well as the O atom of THF, is coordinated to two cations (Figure 1). Atoms S and K lie in the crystallographic plane *bc*, atoms K form chains along the *b* axis with K···K distances of 373.2 pm (effective ionic radius of K^+ is 138 pm for coordination number 6). The layers formed by alternating molecules of **1** and THF can be identified in the crystal as well (Figure 2).



1 **2** **3**

Scheme 1

As compared with **2**,[11] the SN bonds in **1** (Figure 1) are noticeably elongated, and the C(5)–C(6) bond is shortened (Figure 1). This is in agreement with the structure of the π-SOMO of **1** emerging from ROHF/6-31G(d) calculations (Figure 3).

Theoretical calculations of the dimeric exchange interactions (J_i) performed for experimental crystal packing of **3** using a spin-unrestricted broken-symmetry approach at the DFT/UB3LYP/6-31+G(d) level of theory [(*cf.* refs. 7(*a*),(*c*)][§] allow some

† *Preparation of salt* **3**. Under anaerobic conditions in an H-shaped Schlenk vessel equipped with two Teflon valves (vertical tubes) and a G4 frit (horizontal tube) 0.14 g (0.001 mol) of **2** (Aldrich) was added to a suspension of 0.08 g (0.002 mol) of potassium in 10 ml of THF, and the reaction mixture was stirred at ambient temperature for 10 days. During this time colour of the solution changed from pale yellow to crimson and a red-brown precipitate formed. The solution was filtered through the frit to another tube, and the solvent was condensed back by cooling the reaction tube in an ice bath. These operations were repeated several times until extraction of poorly soluble **3** was completed. Red-brown microcrystalline **3** (0.14 g, 57%) was then separated from supernatant solution and dried *in vacuo*. Found (%): C, 48.03; H, 4.63; N, 11.85. Calc. for $C_{10}H_{12}KN_2OS$ (%): C, 48.55; H, 4.89; N, 11.32. Single crystals suitable for X-ray diffraction were obtained by keeping the mother liquor at 7 °C.

‡ *XRD data for salt* **3**: $C_{10}H_{12}KN_2OS$, $M = 247.38$, monoclinic, space group $P2/c$, $a = 12.049(2)$, $b = 6.456(1)$ and $c = 14.915(2)$ Å, $\beta = 96.73(1)°$, $V = 1152.14$ Å^3, $Z = 4$, $d_{calc} = 1.426$ g cm^{-3}, μ(MoKα) = 0.62 mm^{-1}. The final indices are $wR_2 = 0.0802$, $S = 0.960$ for all 1816 F^2, $R_1 = 0.0381$ for 1227 $F_0 > 4\sigma F_0$ (138 parameters). The data were measured at 203(2) K on a Stoe IPDS diffractometer using MoKα ($\lambda = 71.073$ pm) radiation with a graphite monochromator. The structure was solved by the direct methods using the SHELXS-97 program[13] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation by use of the SHELXL-97 program.[13]

CCDC 695223 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

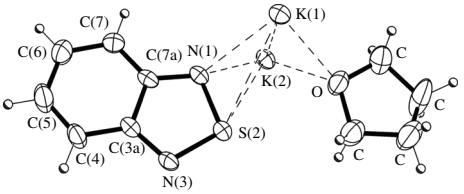


Figure 1 Orientation of the nearest ions in the crystal of **3**. Of two crystallographically unique cations, K(1) lies on the C_2 axis and K(2) at the centre of symmetry, with the site occupation factors of 0.50. Selected bond lengths (pm) and bond angles (°) of **1** (in parentheses, those of **2**[11]): N(1)–S(2) 166.9(3) (162.0), S(2)–N(3) 165.5(2) (161.4), N(3)–C(3a) 135.5(4) (134.8), C(3a)–C(4) 140.0(4) (141.9), C(4)–C(5) 136.9(5) (137.0), C(5)–C(6) 138.5(4) (142.8), C(6)–C(7) 139.5(4) (136.6), C(7)–C(7a) 138.9(5) (141.7), C(7a)–N(1) 137.0(4) (135.2), C(7a)–C(3a) 143.9(3) (144.1); C(7a)–N(1)–S(2) 106.0(2) (106.4), N(1)–S(2)–N(3) 99.8(1) (101.1), S(2)–N(3)–C(3a) 106.4(2) (106.5), N(3)–C(3a)–C(7a) 114.4(2) (113.3), C(3a)–C(7a)–N(1) 113.4(2) (112.8). Non-bonding distances (pm): N(1)···K(1) 295.6(3), N(1)···K(2) 290.7(2), S(2)···K(1) 344.5(1), S(2)···K(2) 354.6(1), O···K(1) 283.3(2), O···K(2) 289.1(2), K(1)···K(2) 373.2(4). Selected bond lengths (pm) and bond angles (°) of **1** from DFT/UB3LYP/6-31G(d) calculations: N(1)–S(2) 170.6, S(2)–N(3) 170.6, N(3)–C(3a) 135.1, C(3a)–C(4) 141.6, C(4)–C(5) 139.8, C(5)–C(6) 140.5, C(6)–C(7) 139.8, C(7)–C(7a) 141.6, C(7a)–N(1) 135.1, C(7a)–C(3a) 146.1; C(7a)–N(1)–S(2) 105.0, N(1)–S(2)–N(3) 99.8, S(2)–N(3)–C(3a) 105.0, N(3)–C(3a)–C(7a) 115.1, C(3a)–C(7a)–N(1) 115.1.

preliminary comments on the magnetic structure of this salt to be made. The structure seems to be unexpectedly complex [*cf.* refs. 7(*a*),(*c*)]. In particular, 12 unique J_i values of both signs were found corresponding to both antiferromagnetic (negative) and ferromagnetic (positive) interactions (Figure 4, Table 1). This situation highlights the importance of quantum chemical calculations for a decent understanding of magnetic properties

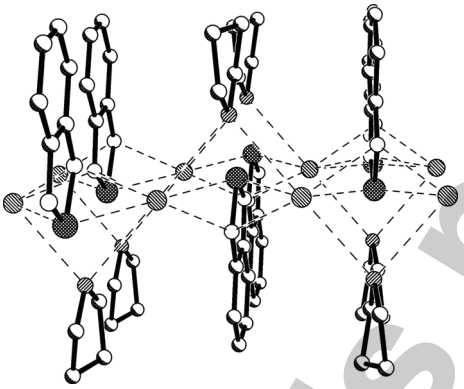


Figure 2 Crystal packing of the salt **3**.

§ *Quantum chemical calculations on* **1** *and* **3**. All calculations were performed using GAUSSIAN-03 suite of programs.[14] The geometry of radical anion **1** was optimized at the DFT/(U)B3LYP/6-31G(d) level of theory.[15] The hfc constants were calculated by the same method. The π-SOMO orbital of the **1** was characterized at the ROHF level of theory.

For theoretical analysis of the magnetic structure of the salt **3** we used a Heisenberg Hamiltonian as given by the equation (1).

$$\hat{H} = -2\sum_{A,B}^{N} J_{AB}\hat{S}_A\hat{S}_B. \quad (1)$$

The exchange integrals (J_{AB}) between selected pairs of radical anions **1** were calculated for the XRD crystal structure of **3** using the spin-unrestricted broken-symmetry approach[16] at the DFT/UB3LYP/6-31+G(d) level of theory.[15] The J_{AB} values were obtained from the equation (2), where E^T is the energy of the triplet state of the pair of radical anions, and E^S_{BS} is the energy of the open-shell singlet state within the broken-symmetry approach.[16]

$$J_{AB} = E^S_{BS} - E^T. \quad (2)$$

In all cases the $<S^2>$ value for the broken-symmetry singlet state was ~1.02. The accuracy of the energy calculations was chosen to be 10^{-7} H which provided calculations of J_{AB} with the accuracy of 0.04 cm^{-1}.

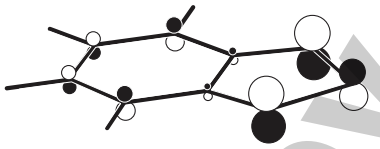


Figure 3 The π-SOMO of radical anion **1** from ROHF/6-31G(d) calculations.

of non-common derivatives:[12] since the exchange interactions of different signs would compensate each other, the magnetic structure of **3** cannot be obtained from magnetic measurements alone. Due to these findings, the magnetic properties of salt **3** are worth of further experimental and theoretical studies. The results of these studies will be published elsewhere.

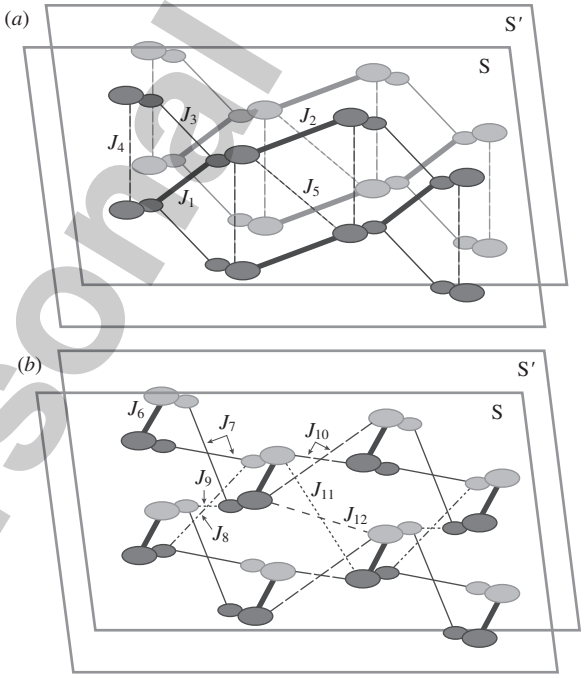


Figure 4 Magnetic structure of salt **3** from the spin-unrestricted broken-symmetry DFT/UB3LYP/6-31+G(d) calculations (see also Table 1). The 5- and 6-membered rings of **1** are represented by the smaller and bigger circles, respectively; dark-gray radical anions **1** occupy layer S, and light-gray ones layer S′. (*a*) The exchange integrals (J_{AB}) between the unique pairs of **1** located in same layer of radical anions **1** (S or S′). (*b*) The exchange integrals (J_{AB}) between the unique pairs of **1** located in adjacent layers of radical anions **1** (S and S′).

We are grateful to Professor Ruediger Mews for valuable discussions.

This work was supported by the Deutsche Forschungsgemeinschaft (grant no. 436 RUS 113/967/0-1R) and the Siberian Branch of the Russian Academy of Sciences (interdisciplinary project no. 25).

Table 1 Spin-unrestricted broken-symmetry results obtained at the DFT/UB3LYP/6-31+G(d) level of theory for the dimeric exchange interaction J_i (Figure 4) of the radical anion **1** with first-nearest neighbours in the crystal of salt **3**.

Exchange interaction	d(S···S)/pm	J_i/cm^{-1}	Exchange interaction	d(S···S)/pm	J_i/cm^{-1}
J_1	373	7.2	J_7	748	–0.07
J_2	1256	–8.1	J_8	709	<|0.04|
J_3	379	3.2	J_9	780	–0.09
J_4	747	–1.0	J_{10}	1412	–0.04
J_5	1335	–0.15	J_{11}	1465	<|0.04|
J_6	645	–0.3	J_{12}	1501	–0.07

References

1 (*a*) C. M. Robertson, D. J. T. Myles, A. A. Leitch, R. W. Reed, B. M. Dooley, N. L. Frank, P. A. Dube, L. K. Thompson and R. T. Oakley, *J. Am. Chem. Soc*., 2007, **129**, 12688; (*b*) A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube and R. T. Oakley, *Chem. Commun*., 2007, 3368; (*c*) A. A. Leitch, R. W. Reed, C. M. Robertson, J. F. Britten, X. Yu, R. A. Secco and R. T. Oakley, *J. Am. Chem. Soc*., 2007, **129**, 7903; (*d*) J. L. Brusso, K. Cvrkalj, A. A. Leitch, R. T. Oakley, R. W. Reed and C. M. Robertson, *J. Am. Chem. Soc*., 2006, **128**, 15080; (*e*) J. L. Brusso, S. Derakhshan, M. E. Itkis, H. Kleinke, R. C. Haddon, R. T. Oakley, R. W. Reed, J. F. Richardson, C. M. Robertson and L. K. Thompson, *Inorg. Chem*., 2006, **45**, 10958; (*f*) L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, R. T. Oakley, R. W. Reed, J. F. Richardson, R. A. Secco and X. Yu, *Chem. Commun*., 2005, 5745.

2 (*a*) K. Awaga, T. Tanaka, T. Shirai, Y. Umezono and W. Fujita, *C. R. Chimie*, 2007, **10**, 52; (*b*) K. Awaga, T. Tanaka, T. Shirai, M. Fujimori, Y. Suzuki, H. Yoshikava and W. Fujita, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 25; (*c*) K. Okamoto, T. Tanaka, W. Fujita, K. Awaga and T. Inabe, *Angew. Chem., Int. Ed. Engl*., 2006, **45**, 4516.

3 (*a*) M. Deumal, S. LeRoux, J. M. Rawson, M. A. Robb and J. J. Novoa, *Polyhedron*, 2007, **26**, 1949; (*b*) J. M. Rawson, A. Alberola and A. Whalley, *J. Mater. Chem*., 2006, **16**, 2560; (*c*) J. M. Rawson, J. Luzon and F. Palacio, *Coord. Chem. Rev*., 2005, **249**, 2631; (*d*) M. Mito, T. Kawae, K. Takeda, S. Takagi, Y. Matsushida, H. Deguchi, J. M. Rawson and F. Palacio, *Polyhedron*, 2001, **20**, 1509; (*e*) J. M. Rawson and F. Palacio, *Struct. Bonding (Berlin)*, 2001, **100**, 93; (*f*) J. M. Rawson and G. D. MacManus, *Coord. Chem. Rev*., 1999, **189**, 135.

4 (*a*) K. V. Shuvaev, A. Decken, F. Grein, T. S. M. Abedin, L. K. Thompson and J. Passmore, *Dalton Trans*., 2008, 4029; (*b*) T. S. Cameron, A. Decken, R. M. Kowalczyk, E. J. L. McInnes, J. Passmore, J. M. Rawson, K. V. Shuvaev and L. K. Thompson, *Chem. Commun*., 2006, 2277; (*c*) A. Decken, S. M. Mattar, J. Passmore, K. V. Shuvaev and L. K. Thompson, *Inorg. Chem*., 2006, **45**, 3878; (*d*) T. S. Cameron, M. T. Lemaire, J. Passmore, J. M. Rawson, K. V. Shuvaev and L. K. Thompson, *Inorg. Chem*., 2005, **44**, 2576; (*e*) G. Antorrena, S. Brownridge, T. S. Cameron, F. Palacio, S. Parsons, J. Passmore, L. K. Thompson and F. Zarlaida, *Can. J. Chem*., 2002, **80**, 1568.

5 (*a*) K. E. Preuss, *Dalton Trans*., 2007, 2357; (*b*) N. G. R. Hearns, K. D. Hesp, M. Jennings, J. L. Korcok, K. E. Preuss and C. S. Smithson, *Polyhedron*, 2007, **26**, 2047; (*c*) M. Jennings, K. E. Preuss and J. Wu, *Chem. Commun*., 2006, 341.

6 (*a*) R. T. Boere, A. M. Bond, T. Chivers, S. W. Feldberg and T. L. Roemmele, *Inorg. Chem*., 2007, **46**, 5596; (*b*) R. T. Boere, H. M. Tuononen, T. Chivers and T. L. Roemmele, *J. Organomet. Chem*., 2007, **692**, 2683; (*c*) R. T. Boere and T. L. Roemmele, *Coord. Chem. Rev*., 2000, **210**, 369.

7 (*a*) S. N. Konchenko, N. P. Gritsan, A. V. Lonchakov, I. G. Irtegova, R. Mews, V. I. Ovcharenko, U. Radius and A. V. Zibarev, *Eur. J. Inorg. Chem*., 2008, 3833; (*b*) N. P. Gritsan, A. V. Lonchakov, E. Lork, R. Mews, E. A. Pritchina and A. V. Zibarev, *Eur. J. Inorg. Chem*., 2008, 1994; (*c*) I. Yu. Bagryanskaya, Yu. V. Gatilov, N. P. Gritsan, V. N. Ikorskii, I. G. Irtegova, A. V. Lonchakov, E. Lork, R. Mews, V. I. Ovcharenko, N. A. Semenov, N. V. Vasilieva and A. V. Zibarev, *Eur. J. Inorg. Chem*., 2007, 4751; (*d*) V. N. Ikorskii, I. G. Irtegova, E. Lork, A. Yu. Makarov, R. Mews, V. I. Ovcharenko and A. V. Zibarev, *Eur. J. Inorg. Chem*., 2006, 3061; (*e*) A. Yu. Makarov, I. G. Irtegova, N. V. Vasilieva, I. Yu. Bagryanskaya, T. Borrmann, Yu. V. Gatilov, E. Lork, R. Mews, W.-D. Stohrer and A. V. Zibarev, *Inorg. Chem*., 2005, **44**, 7194.

8 (*a*) Z. V. Todres, *Organic Ion Radicals. Chemistry and Applications*, Marcel Dekker, Basel, 2003; (*b*) I. Gallardo, G. Guirado, J. Marquet and N. Vila, *Angew. Chem., Int. Ed. Engl*., 2007, **46**, 1321; (*c*) M. S. Denning, M. Irwin and J. Goicoechea, *Inorg. Chem*., 2008, **47**, 6118.

9 A. F. Cozzolino, N. E. Gruhn, D. L. Lichtenberger and I. Vargas-Baca, *Inorg. Chem*., 2008, **47**, 6220.

10 C. L. Kwan, M. Carmack and J. K. Kochi, *J. Phys. Chem*., 1976, **80**, 1786.

11 T. Suzuki, T. Tsuji, T. Okubo, T. Okada, Y. Obana, T. Fukushima, T. Miyashi and Y. Yamashita, *J. Org. Chem*., 2001, **66**, 8954.

12 E. V. Gorelik, V. I. Ovchareko and M. Baumgarten, *Eur. J. Inorg. Chem*., 2008, 2837.

13 G. M. Sheldrick, *SHELX-97 – Programs for Crystal Structure Analysis (Release 97-2)*, University of Göttingen, Germany, 1997.

14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision B.02)*, Gaussian Inc., Pittsburgh, PA, 2003.

15 (*a*) P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev*., 2003, **103**, 1793; (*b*) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648; (*c*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

16 (*a*) L. Noodleman, *J. Chem. Phys*., 1981, **74**, 5737; (*b*) L. Noodleman and E. R. Davidson, *Chem. Phys*., 1986, **109**, 131; (*c*) L. Noodleman, D. A. Case and J. M. Mouesca, *Coord. Chem. Rev*., 1995, **144**, 199; (*d*) H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka and K. Yamaguchi, *Coord. Chem. Rev*., 2000, **198**, 265.

Received: 21st July 2008; Com. 08/3185