

# Trans-dichloro-tris([5]trovacenyl)stannate(IV), electro- and magneto-communication across a Cl–Sn–Cl backbone†

Christoph Elschenbroich,\* Feng Lu, Olav Burghaus, Clemens Pietzonka and Klaus Harms

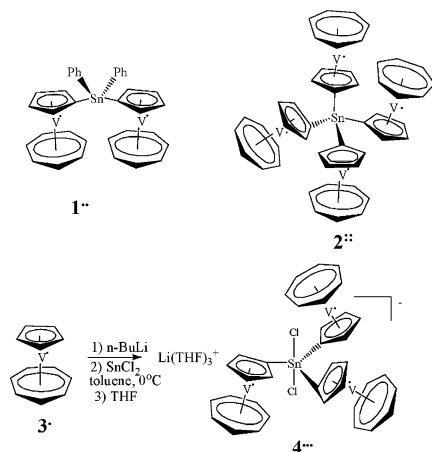
Received (in Cambridge, UK) 6th March 2007, Accepted 10th May 2007

First published as an Advance Article on the web 23rd July 2007

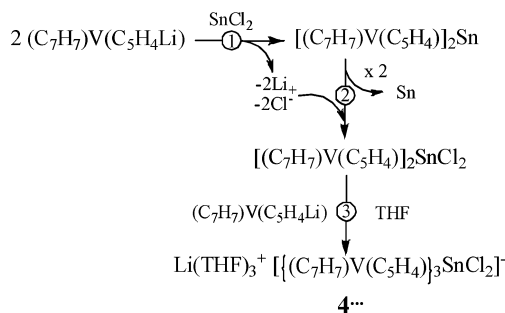
DOI: 10.1039/b703349d

Reaction of [5]lithiotrovacene (TVC-Li) with tin dichloride affords the triradical complex  $(\text{THF})_3\text{Li}^+[(\text{TVC})_3\text{SnCl}_2]^-$  which was characterized by X-ray crystallography, cyclic voltammetry, EPR spectroscopy and magnetic susceptometry; redox splittings  $\delta E_{1/2}$  (“electrocommunication”) and the exchange parameters  $J_{\text{EPR}}$  and  $J_x$  (“magneto-communication”) attest to inter vanadium interactions mediated by the central tin atom.

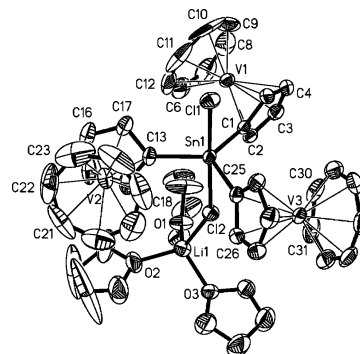
The interest in linked metallocenes is multifarious, it ranges from fundamental questions concerning metal–metal interactions in dimetallocenyls<sup>2</sup> to materials properties exhibited by polymetallocenyls.<sup>3</sup> Often, information gained for small oligometallocenes triggers attempts to transfer features such as intermediate-valence character, *i.e.* very fast intramolecular electron transfer, or spin exchange coupling to the corresponding macromolecules in order to endow them with desirable properties like electrical conductivity or molecular ferromagnetism. In this endeavour a decisive role is played by the spacers between individual metallocene units as they modulate the extent of intermetallic interaction.<sup>2,4</sup> We have recently prepared the di- and tetra([5]trovacenyls) **1<sup>••</sup>** and **2<sup>••</sup>** in which ( $\eta^7$ -tropylium)vanadium ( $\eta^5$ -cyclopentadienyl) (TVC) units are linked by a Sn atom.<sup>1</sup> In this communication we report on the compound **4<sup>•••</sup>** where Sn is connected to three [5]trovacenyl units in a species of trigonal bipyramidal symmetry. Trovacene **3<sup>•</sup>** which contains low spin V( $d^5$ ) is an essentially metal-centered organo-metallic radical.<sup>2b</sup>



Ironically, **4<sup>•••</sup>** was obtained from a reaction that was carried out with totally different target compounds in mind, namely di([5]trovacenyl)stannylene or its dimer tetra([5]trovacenyl)distanylene. Monolithiation of trovacene **3<sup>•</sup>** and subsequent reaction with  $\text{SnCl}_2$  affords the salt lithium dichloro-tris([5]trovacenyl)stannate(IV) **4<sup>•••</sup>** in moderate yield (Scheme 1†). Since oxidizing reagents are absent, the formation of a Sn(IV) complex from a Sn(II) precursor must involve a disproportionation step 2 as delineated in the following tentative scheme:



While this formation of an organotin(IV) compound from a stannylene *via* disproportionation to our knowledge is without precedent, a parallel can be seen in the documented disproportionation of plumbylene intermediates,  $2\text{PbR}_2 \rightarrow \text{PbR}_4 + \text{Pb}$ .<sup>5</sup> The molecular structure of **4<sup>•••</sup>** was determined by X-ray diffraction, a view is presented in Fig. 1§, important bond lengths and angles are collected in the caption. As usual for  $\text{R}_3\text{SnCl}_2^-$  anions, the organic



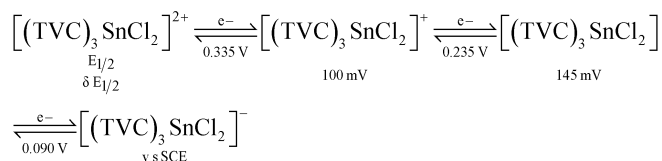
**Fig. 1** Molecular structure of dichloro-tris([5]trovacenyl)stannate(IV) **4<sup>•••</sup>** in the crystal (50% probability ellipsoids). Selected bond lengths (Å) and angles [°]: Sn(1)–C(1) 2.128(2), Sn(1)–C(13) 2.130(3), Sn(1)–C(25) 2.130(2), O(1)–Li(1) 1.929(5), Li(1)–O(2) 1.915(5), Li(1)–O(3) 1.938(6), Li(1)–Cl(2) 2.316(5), C(1)–Sn(1)–Cl(1) 91.49(7), C(1)–Sn(1)–C(25) 118.10(9), C(1)–Sn(1)–C(13) 122.68(10), Cl(1)–Sn(1)–Cl(2) 178.51(2), Li(1)–Cl(2)–Sn(1) 150.89(13), V(1)···V(2) 6.8630(08), V(1)···V(3) 6.7364(42), V(2)···V(3) 6.7612(578).

Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany. E-mail: eb@chemie.uni-marburg.de; Fax: +49 6421 2825653; Tel: +49 6421 2825527

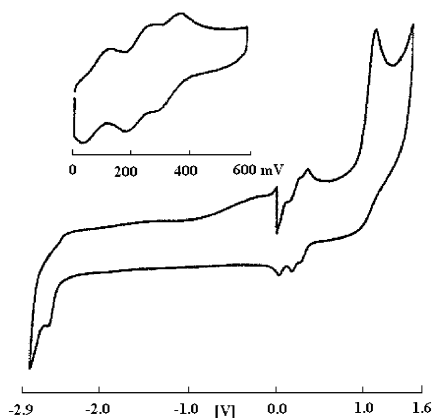
† Trovacene Chemistry, Part 15; for Part 14, see ref. 1.

substituents in  $4^{***}$  assume the equatorial positions of the trigonal bipyramid and the Cl–Sn–Cl axis is practically linear ( $178.5^\circ$ ). The bond length Sn1–Cl2 (2.69 Å) considerably exceeds the value for Sn1–Cl1 (2.51 Å), which is plausible because Cl1 also coordinates to  $[(\text{THF})_3\text{Li}]^+$ . The dimensions of the trovacenyl units in  $4^{***}$  differ only marginally from those in parent  $3^*$ . The dihedral angles of cyclopentadienyl ring planes, and the central triangle C1–C13–C25 amount to  $72.8^\circ$  for TVC(1),  $75.34^\circ$  for TVC(2) and  $77.68^\circ$  for TVC(3). Sn1 is positioned  $0.07$  Å above the plane C1–C13–C25, away from the  $\text{Li}^+$  coordinated Cl ligand. Presumably, in solution ion pairing will be broken and a more symmetrical structure is adopted by the anion  $\{[(\text{C}_7\text{H}_7)\text{V}(\text{C}_5\text{H}_4)]_3\text{SnCl}_2\}^-$ . This association may also be responsible for the fact that twisting of the ligands in the equatorial plane is much more severe for  $[(\text{THF})_3\text{Li}]^+[(\text{TVC})_3\text{SnCl}_2]^-$  than for  $[\text{Ph}_3\text{AsCH}_2\text{COPh}]^+[\text{Ph}_3\text{SnCl}_2]^-$ <sup>6</sup> where ion pairing is suppressed by the bulky cation.

Electrocommunication generally expresses itself in the gradation of electrochemical potentials characterizing successive redox steps in oligonuclear complexes. In the case of  $4^{***}$  cyclic voltammetry (Fig. 2) generates the three-step sequence:



The redox splittings for these vanadium centered redox processes conform to those found for other di-, tri- and tetra[5]trovacenyls featuring one-atom spacers. The first oxidation step  $(\text{TVC})_3\text{SnCl}_2^{-/0}$  is cathodically shifted by 170 mV relative to  $E_{1/2}(\text{TVC}^{+/0}) = 0.26$  V.<sup>7</sup> This is plausible in view of the negative total charge of the former species. Consequently, the potential for the second step, which represents the oxidation of neutral  $[(\text{TVC})_3\text{SnCl}_2]$ , mimics that of parent TVC  $3^*$ . Oxidation of positively charged  $[(\text{TVC})_3\text{SnCl}_2]^+$  then occurs at more positive potential than that of parent TVC. Reduction of  $[(\text{TVC})_3\text{SnCl}_2]^-$  sets in at  $E \approx -2.49$  V, but the proximity to the cathodic border of the medium and the limited reversibility prevent observation of



**Fig. 2** Cyclic voltammograms of  $[(\text{TVC})_3\text{SnCl}_2]^{3-}$  in DME–TBAP at  $-40$  °C, SCE reference electrode,  $\nu = 100$  mV s<sup>-1</sup>,  $E_{1/2}(0/-) = 0.090$  V,  $\Delta E_p = 78$  mV,  $r = 1$ ;  $E_{1/2}(+/0) = 0.235$  V,  $\Delta E_p = 87$  mV,  $r = 1$ ,  $\delta E_{1/2}(+/0, 0/-) = 145$  mV;  $E_{1/2}(2+/+) = 0.335$  V,  $\Delta E_p = 82$  mV,  $r = 1$ ;  $\delta E_{1/2}(2+/+, +/0) = 100$  mV;  $E_{\text{pa}} = 1.14$  V;  $E_{\text{pc}} = -2.49$  V.

a three-step reaction cascade. Since reduction at the TVC unit of  $[(\text{TVC})_3\text{SnCl}_2]^-$  would be expected to be shifted cathodically relative to  $E_{1/2}(\text{TVC}^{0/-}) = -2.55$  V,<sup>7</sup> the wave at  $E \approx -2.49$  V may well represent reduction at central Sn(IV). The large cathodic peak current also suggests that a redox couple chemically different from trovacene<sup>0/-</sup> is involved here. In the absence of suitable reference molecules, this supposition is difficult to substantiate, though.

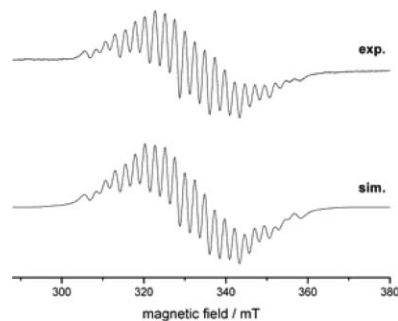
Magnetocommunication in oligonuclear paramagnets is discernable from the hyperfine pattern in EPR spectra as well as from temperature dependent magnetic susceptibility. If trovacene  $3^*$  serves as a probe, the former approach covers the range  $0.001 < |J| < 1.0$  cm<sup>-1</sup>,<sup>4a</sup> whereas the latter is applicable for  $|J| \geq 1$  cm<sup>-1</sup>, depending on the lowest temperature accessible in the experiment. The EPR spectrum of  $4^{***}$  in fluid solution shown in Fig. 3 exhibits a 22 line <sup>51</sup>V hyperfine pattern in which the splitting amounts to  $a(^{51}\text{V}, 3^*)/3$ . The intensity distribution approaches the 1 : 2...10 : 11 : 11 : 10... 2 : 1 sequence. This is to be expected for an equilateral triangular disposition of electron spins located on <sup>51</sup>V nuclei whereby for the exchange coupling constant the relation  $|J_{\text{iso}}| \gg a_{\text{iso}}(^{51}\text{V})$  applies. For a general triad of spins the isotropic spin hamiltonian is given by:

$$\hat{H} = \mu_B \sum_{i=1-3} g_{\text{iso}}^i S_{zi} + \sum_{i=1-3} a_{\text{iso}}^i \vec{I}_i - \sum_{i < j=1-3} J_{\text{iso}}^{ij} \vec{S}_i \vec{S}_j$$

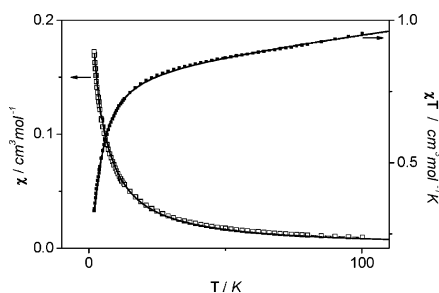
For symmetry reasons in the case of  $4^{***}$   $J^{12} \approx J^{13} \approx J^{23}$  and a single  $J_{\text{iso}}$  parameter applies; satisfactory agreement is obtained if the spectrum in Fig. 3 is simulated to first order by means of the parameter  $|J_{\text{iso}}| = 0.5$  cm<sup>-1</sup>. This value is considerably smaller than that observed for the diradical  $\{(\text{C}_7\text{H}_7)\text{V}(\text{C}_5\text{H}_4)\}_2\text{SnPh}_2$  ( $1^{**}$ ),  $|J_{\text{EPR}}(1^{**})| = 1.4$  cm<sup>-1</sup>.<sup>1</sup> A similar gradation had been detected for the pair  $\{(\text{C}_7\text{H}_7)\text{V}(\text{C}_5\text{H}_4)\}_2\text{BMes}$  ( $5^{**}$ ) and  $\{(\text{C}_7\text{H}_7)\text{V}(\text{C}_5\text{H}_4)\}_3\text{B}$  ( $6^{***}$ ).<sup>8</sup> From the  $\chi$ – $T$  dependence (Fig. 4)  $J_\chi(4^{***}) = -1.19$  cm<sup>-1</sup> is derived by means of fitting the experimental data employing the relation:<sup>8,9</sup>

$$\chi_m = \frac{Ng^2\mu_B^2}{2kT} \frac{1 + 5\exp(-3J/kT)}{1 + \exp(-3J/kT)} \frac{T}{(T - \Theta)}$$

Just like the  $J_{\text{EPR}}$  values, the parameters obtained from the susceptibility measurements showed the gradation  $J_\chi(4^{***}) < J_\chi(1^{**})$ . The two couples under discussion  $1^{**}$ ,  $4^{***}$  and  $5^{**}$ ,  $6^{***}$  are presented in Scheme 2 where their  $J_\chi$  and  $J_{\text{EPR}}$  values are also given. It can be seen that the presence of a boron or a tin atom as a spacer results in very similar magnetic behaviour: the equilateral triangular disposition of the V( $d^5$ ) atoms effects weaker exchange interaction compared to a V( $d^5$ ) pair. There is precedent for this



**Fig. 3** EPR spectrum of  $4^{***}$  in fluid solution (THF), 300 K,  $\nu = 9.2101$  GHz.

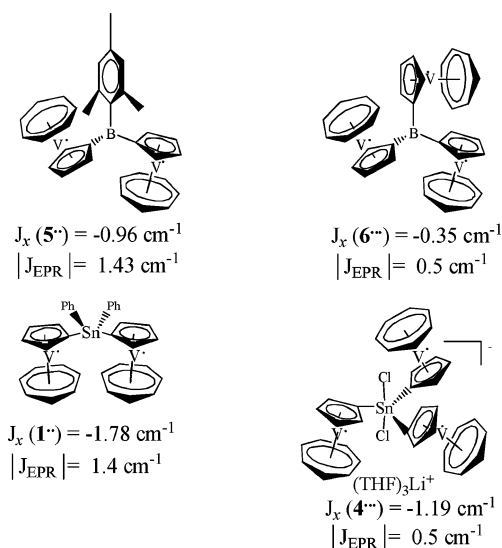


**Fig. 4** Temperature dependence of the magnetic susceptibility  $\chi$  for  $4^{***}$ , presented as  $\chi$  vs.  $T$  and  $\chi T$  vs.  $T$  plots.

observation in that for the couples 1,3,5- $\{(C_7H_7)V(C_5H_4)\}_3C_6H_3$ , 1,3- $\{(C_7H_7)V(C_5H_4)\}_2C_6H_4$ <sup>10</sup> and  $\{(C_5H_5)_2Ti\}_3C_3N_3O_3$ ,  $\{(C_5H_5)_2Ti\}_2C_3HN_2O_2$ ,<sup>11</sup> the triradical also features a smaller exchange parameter  $J$  than the diradical of otherwise identical nature of the spacer. This phenomenon has been interpreted as an expression of spin frustration, which plagues equilateral triradicals if the coupling by its nature is antiferromagnetic.<sup>8,10,12</sup> Because not all three equal spin moments  $S = 1/2$  in equilateral triangular disposition can be aligned antiparallel, this leads to two degenerated doublets as ground state.

Finally, it is conspicuous that the decrease of  $J_{EPR}$  upon going from the diradical to the triradical for the boron as well as for the tin spaced species amounts to approximately 2/3, which also applies to the parameters  $J\chi$  ( $5^{**}$ ) and  $J\chi$  ( $6^{**}$ ). The magnetic susceptibility data for the tin-spaced radicals differ in that the reduction amounts to 1/3 only ( $J\chi$  ( $4^{***}$ )  $\approx$  2/3  $J\chi$  ( $1^{**}$ )). One must consider, though, that the bent  $SnPh_2$  and the linear  $SnCl_2$  units as spacers may not be strictly comparable and more importantly, the magnetic susceptibility for  $4^{***}$  is determined on a solid sample which represents a tight ion pair (see Fig. 1) while the EPR measurement reflects the properties of the solvated triradical anion devoid of lithium contact and probably of slightly different geometry, compared to the solid state.

This work was supported by the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemischen Industrie".



**Scheme 2**

## Notes and references

‡ *Synthesis of  $4^{***}$* : *n*-Butyl lithium (0.9 ml, 1.6 mol l<sup>-1</sup> in hexane) was added to trovacene ( $3^*$ , 270 mg, 1.3 mmol) in diethyl ether (50 ml) and the mixture was stirred at room temperature for 10 h. The red–brown reaction mixture was then added dropwise at 0 °C to a suspension of  $SnCl_2$  (260 mg, 1.39 mmol) in toluene (10 ml). After stirring overnight at room temperature, the yellow solid obtained was washed with Et<sub>2</sub>O till colourless and dried in vacuum. Extraction of this solid with THF–toluene (3 : 1) 30 ml, filtration over Celite and removal of solvent gave 160 mg (yield 47%) of crude  $4^{***}$ . From a portion of the THF–toluene extract which was stored at 8 °C for two months, red–violet prisms were obtained which conformed to the composition  $(THF)_3Li[(TVC)_3SnCl_2] \cdot \frac{1}{2}$  toluene. Recrystallization from THF afforded  $(THF)_3Li[(TVC)_3SnCl_2]$ . MS (EI): *m/z* (relative intensity): 772 ( $[(TVC)_3SnCl]^+$ , 22), 770 ( $[(TVC)_3SnCl]^+-2$ , 100), 326 ( $TVC-Sn^+$ , 5), 207 ( $TVC^+$ , 23). Anal Calcd for  $C_{40}H_{41}Cl_2LiOSnV_3$  (886.783): C, 54.17; H, 4.62. Found: C, 53.85; H, 4.96%. § Crystal data for  $4^{***}$ :  $C_{48}H_{57}Cl_2LiO_3SnV_3 \cdot 0.5C_6H_8O$ ,  $M = 1067.35$ , Triclinic,  $a = 11.6792(13)$  Å,  $b = 13.139(2)$  Å,  $c = 17.1370(19)$  Å,  $\beta = 70.347(9)^\circ$ ,  $V = 2362.2(6)$  Å<sup>3</sup>,  $T = 193(2)$  K, space group  $P\bar{1}$ ,  $Z = 2$ ,  $\mu(Mo-K\alpha) = 0.71073$  mm<sup>-1</sup>, 21625 reflections measured, 8185 unique ( $R_{int} = 0.0417$ ). Final  $R1 = 0.0295$ ,  $wR2 = 0.0804$  (all data). CCDC 641826. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703349d

- C. Elschenbroich, F. Lu, M. Nowotny, O. Burghaus, C. Pietzonka and K. Harms, *Organometallics*, 2007, **26**(14), in press.
- (a) S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637; (b) C. Elschenbroich, O. Schiemann, O. Burghaus, K. Harms and J. Pebler, *Organometallics*, 1999, **18**, 3273.
- (a) V. Chandrasekhar, *Inorganic and Organometallics Polymers*, Springer, Berlin, 2005, ch. 8; (b) I. Manners, *Synthetic Metal Containing Polymers*, Wiley-VCH, Weinheim, 2003.
- (a) C. Elschenbroich, J. Plackmeyer, M. Nowotny, A. Behrendt, K. Harms, J. Pebler and O. Burghaus, *Chem.-Eur. J.*, 2005, **11**, 7427 and previous papers in the series "Trovacene Chemistry"; (b) B. Bildstein, O. Loza and Y. Chizhov, *Organometallics*, 2004, **23**, 1825; (c) W. Skibar, H. Kopacka, K. Wurst, C. Salzmann, K. H. Ongania, F. F. de Biani, P. Zanello and B. Bildstein, *Organometallics*, 2004, **23**, 1024; (d) P. K. A. Shonfield, A. Behrendt, J. C. Jeffery, J. P. Maher, J. A. McCleverty, E. Psillakis, M. D. Ward and C. Western, *J. Chem. Soc., Dalton Trans.*, 1999, 4341; (e) A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K. H. Ongania, K. Wurst and J. P. Launay, *Organometallics*, 1997, **16**, 392; (f) J. P. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386; (g) Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller, K. Scott, L. Koch, N. J. Taylor and T. B. Marder, *J. Organomet. Chem.*, 1993, **452**, 115; (h) A. C. Ribou, J. P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735; (i) K. H. H. Fabian, H. J. Lindner, N. Nimmerfroeh and K. Hafner, *Angew. Chem.*, 2001, **40**, 3517–3520, (*Angew. Chem., Int. Ed.*, 2001, **40**, 3402–3405); (j) J. Classen, R. Gleiter and F. Rominger, *Eur. J. Inorg. Chem.*, 2002, 2040.
- M. Kaupp and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1993, **115**, 1061.
- P. G. Harrison, K. Molloy, R. C. Phillips, P. J. Smith and A. J. Crowe, *J. Organomet. Chem.*, 1978, **160**, 421.
- C. Elschenbroich, E. Bilger and B. Metz, *Organometallics*, 1991, **10**, 2823.
- C. Elschenbroich, M. Wolf, O. Burghaus, K. Harms and J. Pebler, *Eur. J. Inorg. Chem.*, 1999, 2173.
- J. Fujita, M. Tanaka, H. Suemune, N. Koga, K. Matsuda and H. Iwamura, *J. Am. Chem. Soc.*, 1996, **118**, 9347.
- O. Schiemann, J. Plackmeyer, J. Fritscher, J. Pebler and C. Elschenbroich, *Appl. Magn. Reson.*, 2004, **26**, 171.
- B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 1841.
- (a) O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1992; (b) J. S. Miller and M. Drillon, *Magnetism: Molecules to Materials I–V*, Wiley-VCH, Weinheim; (c) H. Y. Woo, H. So and M. T. Pope, *J. Am. Chem. Soc.*, 1996, **118**, 621; (d) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195; (e) V. V. Pavlishchuk, K. S. Gavrilenko and S. V. Kolotilov, *Theor. Exp. Chem.*, 2002, **38**, 21; (f) J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1991, **113**, 3012; (g) J. K. McCusker, C. A. Christmas, P. M. Hagen, R. K. Chadha, D. F. Harvey and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1991, **113**, 6114.