Inorganica Chimica Acta, 189 (1991) 125–128

Inorganica Chimica Acta
LETTER

Sextet ground state in a dinuclear nickel(II) complex containing a tetraoxolene radical as bridging ligand

Andrea Dei, Dante Gatteschi and Luca Pardi
Laboratory of Inorganic Chemistry of the Solid State, Department of Chemistry, University of Florence, Florence (Italy)

(Received September 4, 1991)

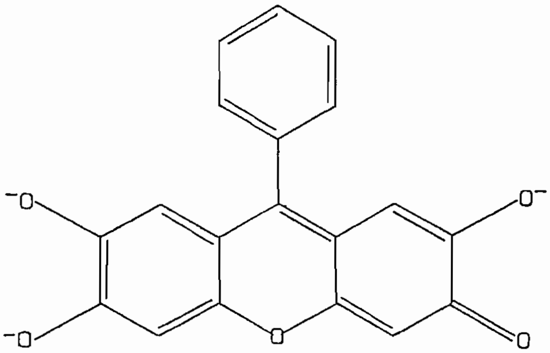
Introduction

We are interested in investigating the interactions between 3d metal ions and polyoxolene radicals, since these derivatives can be in principle used as potential building blocks for synthesizing molecular based ferromagnets. Previous studies on *o*-semiquinonato complexes of these metal ions have shown that both ferro- and antiferromagnetic coupling may be operative within the metal–radical pair [1–8]. However, *o*-semiquinones are rather reluctant to bridge between metal ions [9] and therefore we are extending our interest to tetraoxolene molecules, which in principle may yield radicals acting as bis-bidentate ligands toward metal ions, opening then the possibility of achieving extended networks of metal ions and radicals.

We have recently found that 3d metal ions stabilize the $DHBQ^{3-}$ radical (H_2DHBQ = 2,5-dihydroxy-1,4-benzoquinone) [10]. Solid derivatives of general formula $M_2(CTH)_2(DHBQ)Y_3$ (M = Cr(III), Fe(III); CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Y = ClO_4, PF_6) were isolated and their magnetic properties were found consistent with an $S=5/2$ and $S=9/2$ ground state for chromium(III) and iron(III) derivatives, respectively, as a result of a strong antiferromagnetic coupling between the metal ions and the bridging radical. This finding can be justified with the overlap of the π^* SOMO orbital of the bridging ligand with the t_{2g} orbitals of the metal ions.

The high chemical reactivity of the $M_2(CTH)_2(DHBQ)^+$ complexes, where M is a divalent metal ion, like Mn(II), Fe(II), Ni(II), did not allow us to isolate any reasonably pure solid to afford magnetic characterization. However the determination of the type of magnetic coupling operative in the three spin system Ni(II)–radical–Ni(II) is believed to be important, since on the basis of considerations on the symmetry of the magnetic orbitals of the paramagnetic centers, a ferromagnetic coupling is expected.

With this in mind, we have taken into consideration the molecule 9-phenyl-2,3,7-trihydroxy-6-fluorone



(H_3PTHF) which in principle may act as bis-bidentate ligand in its trianionic form and may yield radical ligands either by one-electron oxidation or by one-electron reduction.

We have synthesized the dinuclear complex $Ni_2(CTH)_2(PTHF)ClO_4$ as well its one-electron oxidation product $Ni_2(CTH)_2(PTHF)(ClO_4)_2$. Here we report and discuss the magnetic and spectral properties of these derivatives.

Experimental

Materials

$Ni(CTH)(ClO_4)_2$ was synthesized according to a previously reported procedure [11]. 9-Phenyl-2,3,7-trihydroxy-6-fluorone (Aldrich) was recrystallized by dimethylformamide–methanol mixtures.

$Ni_2(CTH)_2(PTHF)ClO_4 \cdot CH_2Cl_2 \cdot H_2O$

H_3PTHF (1 mmol) was suspended in 50 ml of a warm solution of $Ni(CTH)(ClO_4)_2$ (2 mmol) in methanol. Solid sodium hydroxide (3 mmol) was added and the resulting mixture was stirred for 0.5 h. A red–brown microcrystalline material was obtained, which was filtered, washed with methanol and then recrystallized from dichloromethane–pentane mixtures. *Anal.* Found: C, 51.42; H, 7.05; N, 9.35. Calc. for $C_{52}H_{85}Cl_3N_8Ni_2O_{10}$: C, 51.78; H, 7.10; N, 9.29%.

0020-1693/91/$3.50

$Ni_2(CTH)_2(PTHF))(ClO_4)_2 \cdot 2H_2O$

A solution of the above compound (0.3 mmol) in acetonitrile (40 ml) was mixed with a solution containing an equimolar amount of silver(I) perchlorate in the same solvent. Silver metal appeared immediately. The suspension was stirred for 0.5 h, filtered and then an aqueous solution of sodium perchlorate was added to the filtrate. The resulting solution was concentrated under reduced pressure until a violet microcrystalline compound began to appear. It was filtered, washed with water and then recrystallized from acetonitrile–diethylether. *Anal.* Found: C, 49.40; H, 6.73; N, 8.73. Calc. for $C_{51}H_{85}Cl_2N_8Ni_2O_{15}$: C, 49.45; H, 6.92; N, 9.05%.

Physical measurements

Physical measurements were carried out as previously described [5].

Results and discussion

The reaction between $Ni(CTH)(ClO_4)_2$ and H_3PTHF in 2/1 ratio under basic conditions yields a compound of formula $Ni_2(CTH)_2(PTHF)ClO_4$. This compound reacts with several oxidizing reagents, i.e. Br_2, I_2, Ag^+, yielding solutions containing the dipositive cation $[Ni_2(CTH)_2(PTHF)]^{2+}$, which can be isolated as solid diperchlorate.

Previous studies on the coordination chemistry of the $Ni(CTH)^{2+}$ moiety have shown that this acceptor easily reacts with bidentate ligands yielding *cis*-octahedral derivatives [12]. In this frame the two complexes $Ni_2(CTH)_2(PTHF)(ClO_4)_n$ ($n=1$, 2) are assumed to contain dinuclear cations in which the nickel ions are bridged by the $PHTF^{n-}$ ligand with the two macrocycles coordinated in a folded configuration in the remaining octahedral coordination sites. We want to show how the electrochemical, electronic spectral, magnetic susceptibility and EPR data concur to describe $Ni_2(CTH)_2(PTHF)ClO_4$ as a Ni(II)–$PTHF^{3-}$–Ni(II) derivative, and $Ni_2(CTH)_2(PTHF)(ClO_4)_2$ as a Ni(II)–$PTHF^{2-}$–Ni(II) complex.

The cyclic voltammetry traces of deaerated acetonitrile solutions of the two complexes are superimposable and show that they undergo two one-electron reversible redox processes at -2.21 and -0.38 V and one not reversible at $+0.40$ V versus the ferrocinium/ferrocene couple. The couple at -0.38 V involves the two species isolated as solid compounds and it is reasonably associated with a tetraoxolene centered redox process as

$$\mathrm{Ni(II)(PTHF^{2-})Ni(II)^{2+}} \overset{+e^-}{\rightleftharpoons} \mathrm{Ni(II)(PTHF^{3-})Ni(II)^{+}}$$

(the CTH coligand is omitted for sake of simplicity) since the oxidation involving the nickel(II) ions is known to occur at significantly more positive potentials [13]. The assignment of the two other redox processes is ambiguous since they may involve either ligand centered or metal centered electron transfer processes.

The electronic spectra of the two isolated species are shown in Fig. 1. The spectrum of $Ni_2(CTH)_2(PTHF)ClO_4$ is dominated by a strong transition at 17 000 cm^{-1} ($\log \epsilon = 4.67$) and two transitions at 26 000 ($\log \epsilon = 3.59$) and 30 800 ($\log \epsilon = 3.89$) cm^{-1}. These bands are assigned to internal transitions of the $PTHF^{3-}$ chromophore by comparison with the spectrum of the H_3PTHF in alkaline medium. The

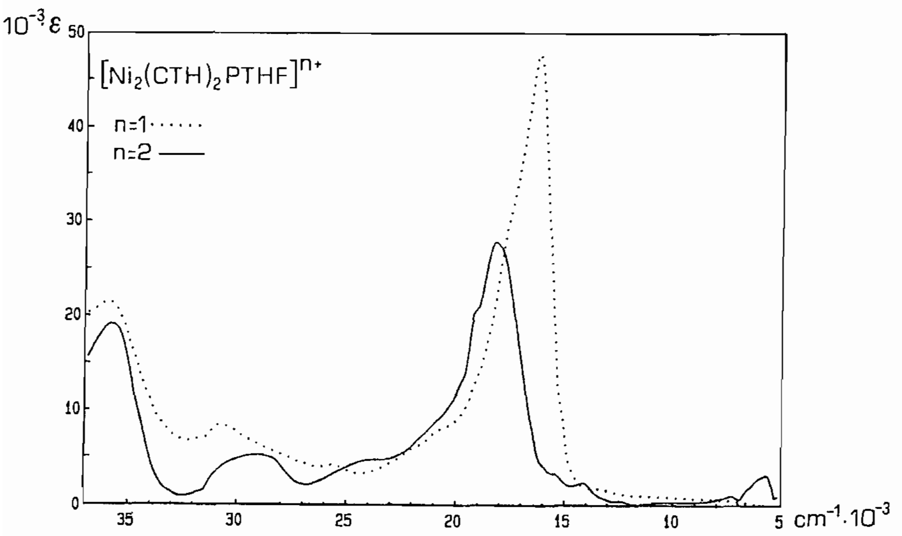


Fig. 1. Electronic spectra of $[Ni_2(CTH)_2(PTHF)]^{n+}$: $n=1$ (·····); $n=2$ (——).

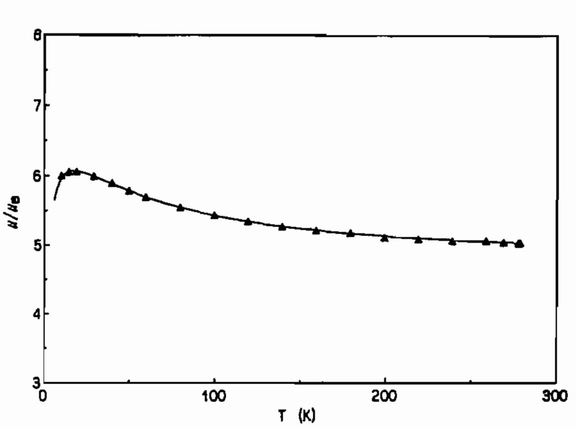


Fig. 2. Variation of magnetic moment with temperature in the range 6–300 K for $Ni_2(CTH)_2(PTHF)(ClO_4)_2 \cdot 2H_2O$. The curve represents the best fit (see text).

spectrum of the one-electron oxidized derivative $Ni_2(CTH)_2(PTHF)(ClO)_2$ shows significant differences. Indeed in addition to the bands at 18 200 (log $\epsilon = 4.44$), 24 000 (log $\epsilon = 3.67$) and 29 000 (log $\epsilon = 3.69$) cm^{-1}, to be assigned as above, the spectrum is characterized by a pattern of bands at 6000 (log $\epsilon = 3.48$), 14 200 (log $\epsilon = 3.36$) and 15 500 (log $\epsilon = 3.50$) cm^{-1}, respectively, which can be reasonably assigned to transitions involving the internal levels of the tetraoxolene and the single occupied molecular orbital (SOMO) of the ligand itself. The observed pattern of bands is fully consistent with the existence of a $PTHF^{2-}$ radical bridging the two metal ions.

The $Ni_2(CTH)_2(PTHF)ClO_4 \cdot CH_2Cl_2 \cdot H_2O$ derivative is paramagnetic with a room temperature effective magnetic moment of 4.35 μ_B, which does not vary on decreasing temperature down to liquid nitrogen, and is EPR silent. These data are consistent with the presence of practically uncoupled high spin nickel(II) ions with $g = 2.2$ bridged by the diamagnetic $PTHF^{3-}$.

The room temperature effective magnetic moment of the $Ni_2(CTH)_2(PTHF)(ClO_4)_2 \cdot 2H_2O$ complex is 5.04 μ_B. It increases on decreasing temperature reaching the value of 6.06 μ_B at 20 K, then decreasing to the value of 5.66 μ_B at 6 K (Fig. 2). The EPR spectrum shows a broad feature centered at $g = 4.53$ at 77 K as shown in Fig. 3.

These data concur to indicate that an electronic ground state with $S = 5/2$ is selectively populated at low temperature. In fact an isotropic EPR spectrum with $g = 4.3$ is generally observed in larger rhombic fields [14]. The deviation observed in this case from the expected value may be due to the presence of orbital contribution from the nickel(II) ions. According to this hypothesis, the observed magnetic data were fitted using the exchange Hamiltonian

$$\mathcal{H} = J_{NiNi} S_{Ni} S_{Ni} + 2J_{NiR} S_{Ni} S_R$$

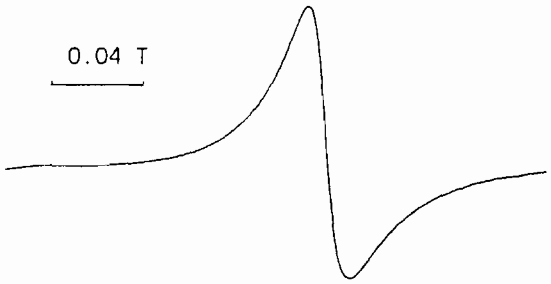


Fig. 3. Polycrystalline powder EPR spectrum of $Ni_2(CTH)_2(PTHF)(ClO_4)_2 \cdot 2H_2O$ at 77 K.

where J_{NiNi} is the coupling constants between the two metal ions, J_{NiR} is the coupling constant between the metal ions and the $PTHF^{2-}$ radical. The decrease of the effective magnetic moment below 20 K can be due either to intermolecular exchange interactions or to zero field splitting within the ground $S = 5/2$ state. We used the latter correction to the spin Hamiltonian in order to fit the experimental susceptibility data. Assuming $J_{NiNi} = 0$ and the g value of the radical equal to 2.00, the best fit parameters were $J_{NiR} = 61(3)$ cm^{-1}, $g_{Ni} = 2.21$, $D = 0.91(2)$ cm^{-1}.

Ferromagnetic coupling between the two high spin nickel(II) ions ($S = 1$) and the radical ($S = 1/2$) induces a sextet electronic ground state for the whole three-spin system. This is the result expected if the magnetic orbitals of the two metal ions are strictly orthogonal to the SOMO of the bridging ligand and the exchange interaction between the metal ions themselves is neglectable. The latter requirement is experimentally verified by the analysis of the magnetic behavior of $Ni_2(CTH)_2(PTHF)^+$, as discussed above, whereas the first would require that the SOMO has π^* character and therefore is orthogonal to the magnetic orbitals of the metal ions, which are σ in character in pseudo-octahedral symmetry. This situation is well known to occur in $Ni(CTH)(SQ)^+$ complexes (SQ = 3,5-di-t-butyl-semiquinonato, tetrachlorosemiquinonato) [5, 6], which are strictly related to the complex under discussion. The smaller value of the exchange coupling constant observed for the present derivatives with respect to those observed for the nickel(II) semiquinonato can be due to some distortion of the coordination polyhedron with a consequent not perfect orthogonality of the magnetic orbitals.

References

1 W. Kaim, *Coord. Chem. Rev., 76* (1987) 187.
2 S. L. Kessel, R. M. Emberson, P. G. Debrunner and D. N. Hendrickson, *Inorg. Chem., 19* (1980) 1170.

3 M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald and C. G. Pierpont, *J. Am. Chem. Soc.*, *106* (1984) 2041.

4 O. Kahn, R. Prins, J. Redijk and J. Thompson, *Inorg. Chem.*, *26* (1987) 3557.

5 C. Benelli, A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, *27* (1988) 2831.

6 C. Benelli, A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, *28* (1989) 1476.

7 C. Benelli, A. Dei, D. Gatteschi, H. U. Güdel and L. Pardi, *Inorg. Chem.*, *28* (1989) 3089.

8 C. Benelli, A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, *29* (1990) 3409.

9 C. G. Pierpont and P. M. Buchanan, *Coord. Chem. Rev.*, *38* (1981) 45.

10 A. Dei, D. Gatteschi, L. Pardi and U. Russo, *Inorg. Chem.*, *30* (1991) 2589.

11 L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, *91* (1969) 4092.

12 N. F. Curtis, D. N. Swann and D. N. Waters, *J. Chem. Soc.*, (1973) 1963.

13 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, *33* (1980) 87.

14 A. Bencini and D. Gatteschi, in B. N. Figgis and G. Melson (eds.), *Transition Metal Chemistry*, Vol. 8, Marcel Dekker, New York, 1982, p. 1.