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A novel discrete dinuclear copper(II)–gadolinium(III) complex derived from a Schiff base ligand [Cu(salbn)Gd$(NO_3)_3 \cdot H_2O$] (salbn): *N*,*N*′-butylenebis(salicylideaminato)

Thekkel M. Rajendiran*
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan – 48109-1055, USA

Ramu Kannappan, Rajaram Mahalakshmi, Rangarajan Venkatesan and Pillutla Sambasiva Rao
Department of Chemistry, Pondicherry University, Pondicherry – 605 014, India

Lakshmanan Govindaswamy and Devadasan Velmurugan
Department of Biophysics Crystallography, University of Madras, Guindy Campus, Madras – 600 025, India

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Abstract

The synthesis, X-ray and e.p.r. spectral studies of a 3d–4f couple are described here. The crystal structure of [Cu(salbn)Gd$(NO_3)_3 \cdot H_2O$], *(2)*, salbn = *N*,*N*′-butylenebis(salicylideaminato), has been determined by X-ray crystallography. Compound *(2)* crystallizes in the monoclinic system, space group p21/n, with $a = 9.025(1)$, $b = 22.912(1)$, $c = 12.790(1)$ Å, $\beta = 99.36(1)$, $Z = 4$. The deviations of the four coordinating atoms (O(1)O(2)N(1) and N(2) of salbn and the copper atom is displaced from the plane in spite of the lack of any apical ligand. The gadolinium(III) ion is nine-coordinated by the two oxygen atoms of the salbn moiety, three bidentate nitrate ions and one water molecule. The geometry of Gd^{III} can be described as a square antiprism, in which compound Cu^{II} and Gd^{III} are bridged by the two phenolic oxygens of salbn. The Cu^{II}–Gd^{III} distance is 3.269(1) Å. The bridging core CuO2Gd is a butterfly shape. Significant distortion was observed for the complex having the larger diamino string. The title compound exhibits seven e.s.r. transitions with $|D| = 0.0467$ cm^{-1}, which demonstrates the existence of zero field splitting. This outcome indicates that compound *(2)* consists of a perfectly isolated dinuclear Cu–Gd core and steric bulk alters the dihedral angle in the Cu–O–Gd bridge.

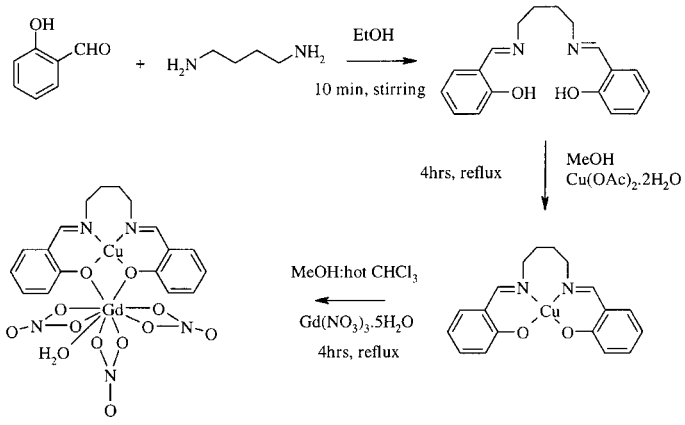
Introduction

The unique properties of copper(II)–gadolinium(III) complexes have attracted increasing interest due to their latent applications in the designs of bimetallic catalysts [1], novel molecular based magnetism and molecule devices [2]. The administration of the contrasting agents in magnetic resonance imaging (MRI) has greatly improved the potentials of this modality [3, 4]. Lanthanide complexes of high stability could turn out to be especially vital in two very different areas of research where inert complexes are potentially useful; namely, for the separation of the lanthanides as a set of metals and for the design of gadolinium(III) contrast agents for n.m.r. imaging [5]. Many medicines require that the complex be inert to metal ion release in water [4]. The MRI contrasting agents have an indirect mode of action. Since they contain paramagnetic metal ions they influence the signal intensity primarily by altering proton relaxation rates in tissue. Gadolinium(III) is the most effective relaxation enhancer and almost all commercially available MRI contrast agents contain gadolinium(III) complexes; important issues in the development of gadolinium(III) containing MRI contrast agent are low toxicity, low osmolality, high thermodynamic and/or kinetic stability and the presence of at least one water molecule in the inner coordination sphere of the Gd metal ion. The coordination chemistry of lanthanides has become of increasing significance in recent years due to the wide variety of potential applications of lanthanide complexes. To date, most of the studies with magnetic properties of 4f–3d complexes have been limited to the copper(II)–gadolinium(III) system. The e.p.r. studies have not been studied in detail so far. In this paper, we describe the synthesis (Scheme 1), crystal structure and e.p.r. spectral studies of gadolinium(III)–copper(II) couple.

Experimental

All chemicals were used as commercially purchased. $Gd(NO_3)_3 \cdot 6H_2O$ was prepared in the usual way by evaporating a solution of the corresponding oxide in HNO_3 to dryness. The ligand [*N*,*N*-1,4-butylethylenebis(salicylaldiminato)] (H_2salbn) was obtained by mixing warm EtOH solutions of salicylaldehyde and 1,4-diaminobutane in a 2:1 molar ratio according to the

* Author for correspondence



Scheme 1.

typical procedure [6, 7]. ^{1}H-n.m.r. (400 MHz) in $CDCl_3$, δ_{ppm}: 8.3(s,2H), 7.3(dd, 2H), 7.2(dd, 2H), 6.9(d, 2H), 6.8(t, 2H), 3.7(t, 4H), 1.9(m, 4H). ^{13}C-n.m.r. (100 MHz) in $CDCl_3$, δ_{ppm}: 165,163, 161, 132, 131, 118, 117, 59 and 28.

Metal presursor Cu(salbn) (1)

To a MeOH solution (50 cm^3) of salbn (0.5 mmol) was added a MeOH solution (25 cm^3) of $Cu(OAc)_2 \cdot 2H_2O$ (0.5 mmol) with stirring. The mixture was subsequently boiled under reflux for 4 h. After cooling to room temperature a green precipitate was collected by filtration, washed with MeOH and dried in air. Yield: 90%. (Found: C, 60.4; H, 5.0; N, 7.8. $C_{18}H_{18}N_2O_2Cu$ calcd.: C, 60.4; H, 5.1; N, 7.8%). Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 358$ (100).

Cu(salbn)Gd(NO$_3$)$_3$·H$_2$O (2)

This compound was prepared by slowly adding a MeOH solution of 0.225 g (0.5 mmol) of $Gd(NO_3)_3 \cdot H_2O$ to a (0.5 mmol) sample of Cu(salbn) dissolved in 100 cm^3 of hot $CHCl_3$ under constant stirring. The mixture was then refluxed for 4 h and the solution was concentrated to 50 cm^3. After slow evaporation, a dark green precipitate was obtained. We attempted to obtain a single crystal suitable for X-ray diffraction The compound was dissolved in hot $CHCl_3$–MeOH mixture under diffusion with Et_2O at room temperature dark green single crystals formed after 3 weeks. Yield: 67%. (Found: C, 29.3; H, 2.7; N, 9.7. $C_{18}H_{20}N_5O_{12}CuGd$ calcd.: C, 30.1; H, 2.8; N, 9.7%).

Physical measurements

^{1}H- and ^{13}C-n.m.r spectra were recorded on a JEOL FX-400 FT-n.m.r. spectrometer in $CDCl_3$ solution, using TMS as the internal standard. I.r. spectra of the complexes and the ligands were recorded on a Hitachi Infrared Spectrophotometer using the KBr pellet technique, in the 4000–200 cm^{-1} range. U.v.–vis. spectra were recorded with an Ocean Optics, Inc., SD 1000 fiber Optic spectrometer in $CHCl_3$ solvent. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/DATA systems using Argon/Xenon (6 kV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol (NBA) as the matrix. Elemental (C, H and N) analyses were performed with a Heraus Rapid analyzer. X-band e.s.r spectra were recorded using a JEOL JES-TE100 ESR Spectrometer.

X-ray structure determination

The crystal of dimensions 0.40 × 0.32 × 0.26 mm (*2*) was glued to a glass fibre. The intensity data were collected at room temperature using the Siemens SMART CCD area detector three-circle diffractometer equipped for graphite monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation. The data collection nominally covered a full hemisphere of reciprocal space by a combination of three sets of exposures, each set having a different ϕ angle for the crystal and each exposure covered 0.3° in ω. The crystal to detector distance was 5.89 cm. Coverage of the unique set was over 86% complete to at least 25.6° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections. Data frames were collected for 10–30 s frames, depending on the intensity of the data, giving an overall time for data collection of 7–18 h. The data frames were integrated using SAINT and were merged to give a unique dataset. The structure was solved by automated Patterson methods and subsequent difference Fourier technique using DIRDIF 98.3. All hydrogen atoms were included at calculated positions using a riding model. The U_{iso} of H atoms of CH and CH_2 groups and the methyl group were taken as $1.2U_{eq}$ of their carrier atoms, except for the water hydrogen atoms, which could not be identified. All non-hydrogen atoms were refined with anisotropic thermal parameters. For the compound, the final *R*-values is 0.063 for 4607 observed reflection with

$I > 2\sigma(I)$ and 0.089 for (6356) all data. Anomalous dispersion effects for all atoms were included in the final calculations.

Results and discussion

Spectral studies

The ligand (salbn) was synthesized by Schiff's base condensation. The spectral studies such as ^{1}H-n.m.r as well as ^{13}C-n.m.r confirms the tetradentate nature of the ligand. The electronic spectrum of the copper(II) complex precursor *(1)* exhibits its higher energy band at 624 nm, while a band red shifted to lower energy at 688 nm for *(2)* seems to be due to a distortion of geometry occurring at the copper center (Figure 1). There is great similarity between the i.r. spectra of the heterodinuclear complexes [8, 9]. They are almost superimposible with the exclusion of the presence of a $\nu_{C=N} = 1645\ cm^{-1}$ in the spectrum of *(2)*. This absorption appears at $\nu_{C=N} = 1638\ cm^{-1}$ in the case of compound *(1)*. In compound *(2)* the energy discrepancy between the asymmetric and asymmetric stretching frequency for (NO_3^-) occurs at $\Delta\nu = 153\ cm^{-1}$, which indicates the nature of bidentate nitrate bridging.

Crystal structure

The unit cell contains four distinct entities of [LCuGd-$(NO_3)_3 \cdot H_2O$]. A view of the dinuclear unit is represented in (Figure 2) with crystal data; selected bond angles and bond lengths given in Tables 1 and 2. The ORTEP diagram of *(2)* is drawn at 50% probability displacement thermal ellipsoids with atomic numbering scheme. The coordination geometry about the Cu ion consists of a chelate ring and a distorted coordination plane composed of two imine N atoms and two phenol O atoms. The copper(II) completes its coordination sphere with two imine nitrogen atoms from the Schiff base. The

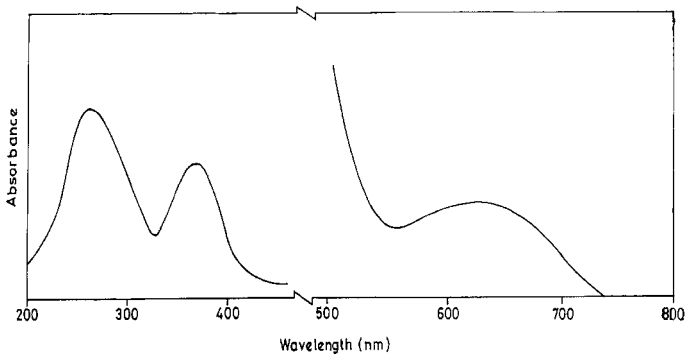


Fig. 1. Electronic spectrum of Cu(salbn)Gd$(NO_3)_3 \cdot H_2O$ *(2)*.

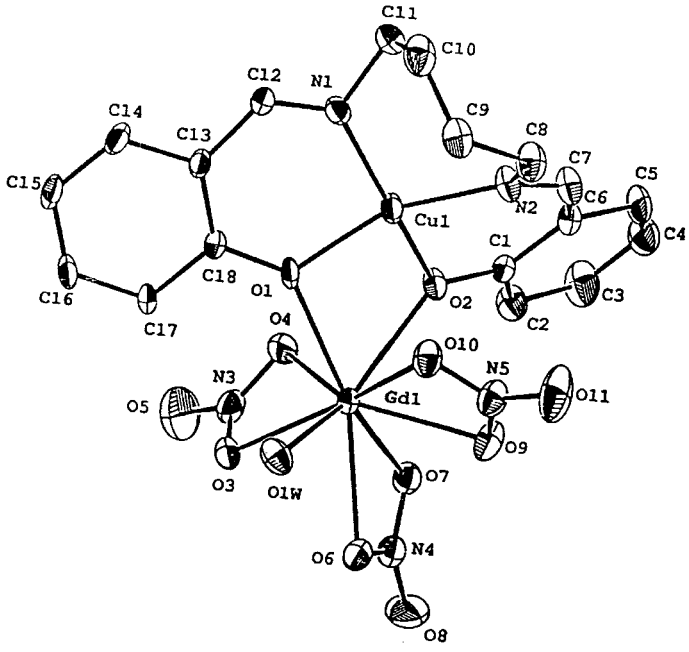


Fig. 2. ORTEP diagram of *(2)* showing the 50% probability thermal ellipsoids.

Table 1. Crystal data for complex *(2)*

Chemical formula	$C_{18}H_{20}N_5O_{12}GdCu$
Chemical formula weight (*Wt*)	719.015
Crystal systems	Monoclinic
Space group	P21/n
Unit cell dimensions (Å^3)	$a = 9.025(1)$ $b = 22.912(1)$ $c = 12.790(1)$
Volume (Å^3)	2609.47(8)
Z	4
Dc (calculated), mg m^{-3}	1.8255
Wavelength, (λ, Å)	0.71073
Absorption coefficient (μ, cm^{-1})	34
Temperature (*T*, K)	294
Crystal size (mm)	$0.40 \times 0.32 \times 0.26$
F(0 0 0)	1400
Data collection	
Diffractometer	Siemens SMART CCD area detector
Index ranges	$-11 \le h \le 12$, $-30 \le k \le 25$, $-16 \le l \le 12$
θ_{max}	28.3°
Reflection measured	20241
Independent reflections	6356
Reflections with $I > 2\sigma(I)$	4607
Refinement	
Refinement method	on *F*2
Reflections used	6356
Refinement parameters	334
Goodness-of-fit (*S*)	1.267
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.064$ & $WR_2 = 0.192$
Largest diff peak and hole (e Å^{-3})	2.74 to −3.95

Table 2. Selected bond distance (Å) and angle (°) for complex *(2)*

Bond lengths			*Bond angles*			
Cu1	Gd1	3.269(1)	Gd	O1	Cu1	97.3(2)
Gd1	O1	2.380(5)	O1	Gd1	O2	67.7(2)
Gd1	O2	2.353(6)	O1	Gd1	O1W	83.4(2)
Gd1	O3	2.463(6)	N1	Cu1	O1	94.4(3)
Gd1	O4	2.541(7)	N1	Cu1	N2	98.7(3)
Gd1	O6	2.510(7)	Gd	O2	Cu1	98.4(2)
Gd1	O7	2.445(6)	O1	Gd1	O4	78.4(2)
Gd1	O9	2.431(7)	O2	Gd1	O7	146.3(2)
Gd1	O10	2.564(6)	N2	Cu1	O2	90.8(3)
Gd1	O1W	2.350(7)	O1	Cu1	O2	84.6(2)
Cu	O1	1.961(6)				
Cu	N1	1.915(7)				
Cu	O2	1.953(5)				
Cu	N2	1.948(7)				

Cu—O bond lengths are 1.961(6) and 1.953(5) Å for Cu—O1 and Cu—O2, respectively while the Cu—N bond lengths are 1.915(7) and 1.948(7) Å for Cu—N and Cu—N2 respectively, which are normal values for gadolinium(II)–copper(II) Schiff base complexes [10–12]; they also agree with previously reported values [13–15]. The most interesting comparative aspects of Cu complexes with imine phenols involve the steric influence of the alkyl backbone upon the molecular structure. The Cu ion is coordinated by two imine nitrogens and two oxygen from the Schiff base ligand. These four atoms deviate significantly from the distorted coordination plane Cu1O1O2N1N2 and they are 0.451(7) and 0.031(1) respectively. The copper is displaced from the plane in spite of the absence of any apical ligand. The steric interaction of the propyl, butyl and phenyl backbones affect the copper coordination geometry significantly in many respects. In the five membered ring systems with a two C atom backbone, the Cu—N distance is short (average 1.916 Å) and the N—Cu—N angle (82.7°) and the dihedral angle (5.3°) are small. Addition of a third C atom to the backbone to make a six membered chelate ring results in increased Cu—N lengths N—Cu—N angles and dihedral angles. Further increase in the backbone size to give a seven membered ring makes it more difficult to maintain the configuration without considerable puckering of the ring. It seems that tuning of the Cu—N lengths, N—Cu—N angle and dihedral contributes to the flexibility of the coordination of copper by tetradentate iminephenol ligands.

Examination of the gauche conformation of the butane bridge, which has often been found to be unsymmetrical, can also provide some basis for comparison of the extent of distortion of copper(II) imine phenol complexes. The butane bridging C atoms are asymmetrical by buckling and its torsion angles are −73(1) (N2—C8—C9—C10), 56(1) (C8—C9—C10—C11) and 50(1)° (C9—C10—C11—N1) respectively. These angles are comparable with similar types of copper(II) coordination complexes [16]. It is well known that increasing the steric hindrance by elongation of the alkyl bridge will result in a change in the chelate pattern from planar to tetrahedral. The distortion of the inner coordination sphere can be recognized by the magnitude of the dihedral angle between the two planes defined by Cu2N2O2. The dihedral angle between two planes is 30.9(2)°.

The gadolinium environment is a distorted square antiprism of oxygen atoms, two belonging to the salbn ligand and six belonging to the three bidentate nitrato ions and one water molecule orientated in axial position. The ninth coordinated water oxygen is at 2.350(7) Å from the gadolinium atom and this value is comparable with the metal H_2O distance observed in other lanthanide complexes: (Gd—O = 2.39(1) Å [7, 11]. The gadolinium(III)–copper(II) distance is 3.269(1) Å, which is close to that 3.252(4) Å, of the complexes of Kahn and co-workers [17] but shorter than those 3.4275(9)–3.5231(4) of the complexes of Costes *et al.* [18] which is still greater than reports by Sasaki *et al.* [19] and Kahn *et al.* [20], the Cu—O2—Gd bridge is asymmetric. The Cu—O bond distances are 0.82 Å shorter than the Gd ones. The two Cu—O—Gd angles are almost equal to each other within an error of 97.3(2) and 98.4(2)°. The three bidentate nitrato ions are bound to the gadolinium(III) ions in a slightly asymmetric fashion. All Gd—O and N—O distances are in good agreement with corresponding values in a similar type of Gd(III)–Ni(II) complex [10]. The evaluation of the dihedral angle

Table 3. Comparison of structural parameters *a* and *b* for dinuclear Cu—Gd complexes

Compound	*a*	*b*	Reference
$LCu(O_2CoMe)Gd(thd)_2$	19.1(2)	3.4727(4)	[21]
$LCu(OCMe_2)Gd(NO_3)_3$	16.6(2)	3.5231(4)	[10]
$LCu(OMe_2)Gd(NO_3)_3$	12.9(2)	3.4275(9)	[17]
$[LCuCl_2Gd(H_2O)_4]Cl \cdot 2H_2O$	1.7(2)	3.5121(5)	[22]
$Salen(Meim)CuGd(hfa)_3$	39.6	3.252(4)	[23]
$Cu(salen)Gd(NO_3)_3 \cdot CH_3OH$	147.4	3.224(1)	[20]
$Cu(salbn)Gd(NO_3)_3 \cdot H_2O$	33.7(2)	3.269(1)	This work
$Cu(salabza)Gd(hfac)_3$	132.61	3.2481(8)	[19]
$[CuLGd(NO_3)_3]$	4.3	3.401	[24]
$[CuGd(ems)(NO_3)_3 \cdot H_2O]$	24.5	3.428(1)	[5]

a is the dihedral angle between the O(1)CuO(2) and O(1)GdO(2) planes in deg and *b* is the Cu—Gd separation in Å. salen = *N*,*N*′-ethylenebis(salicylideaminato). MeIm = 1-methylimidazole. Salbn is described in the text, O_2COMe = monomethyl carbonate, hfac = 1,1,1,5,5,5-hexafluoroacetylacetone and salabza = *N*,*N*′-bis(salicylidene)-2-amino-benzylamine.

and copper(II)–gadolinium(III) distance with previously reported complexes is given in Table 3.

The bridging network GdO1O2Cu has a butterfly shape taking O1O2 as the hinge, the GdO1O2 and CuO1O2 planes forming a dihedral angle of 33.7(2)° and the O1–O2 distance being equal to 2.635(8) Å. These values agree with previously reported results [17]. The O—O distances (O1—O2, O3—O4, O6—O7, O9—O10) fall in the 2.161(10) to 2.635(8) Å range. In accordance with the bidentate nature of NO3 ligands, we note in every case that N—O bond lengths are nearly equal.

Electron paramagnetic resonance

The e.p.r. spectrum of the polycrystalline sample of complex *(1)* has been recorded at 77 K, yielding parameters $g_{\|} = 2.137$, $g_{\perp} = 2.082$, $A_{\|} = 142 \times 10^{-4}$ cm^{-1}. This is typical of tetragonally coordinated monomeric copper(II) complex with the unpaired electron in the dx^2–dy^2 orbital [26]. A polycrystalline powder e.p.r. spectrum of complex *(2)* at room temperature is shown in (Figure 3, insert 1). It shows a strong unique quasi-isotropic broad signals centered at $g = 2.274$ but no clear characteristic peak in the $g = 2$ region [27]. The spectrum of complex *(2)* at 77 K (Figure 3) exhibits an anisotropic broad signal. The spectrum shows a striking temperature dependence and broadens at 77 K [28]. At room temperature the spectrum is uninformative, but on cooling to 77 K, the fine structure exhibits seven transitions around 99, 175, 241, 300, 311, 436 and 465 mT, which may be generated by zero field splitting [29, 30]. This spectrum corresponds to the superposition of the signal of the copper(II) ion, including the gadolinium(III) signal. The weak features 99, 175, 241 and 300 mT obviously leads to an increase in the intensity and the characteristic peak moves toward lower fields, whereas the intense feature at 241 mT becomes wider, due possibly to a spin–spin relaxation effect [31]. This summing up reveals that the copper(II) ($s = 1/2$) gadolinium(III) ($s = 7/2$) interaction is weak which gives rise to an $s = 4$ ground state; $s = 3$ low lying excited state and $s = 4$ may be significantly populated at 77 K.

In this paper, we have described the successful synthesis of a discrete dinuclear complex with increasing backbone chain in the diamine arm which may result from the larger distortion of the geometry around copper(II) towards a tetrahedral structure. The steric interaction of the ethylene, propyl and biphenyl backbones affect the copper coordination geometry significantly in Cu—N distance, N—Cu—N angle and the dihedral angle. Further increase in the backbone size (butyl) to give a seven membered ring makes it more difficult to maintain the configuration without considerable puckering of the ring. Which is tuning the Cu—N lengths, N—Cu—N angle and dihedral angle contributes to the flexibility of the coordination of copper by tetradentate iminophenol ligand. We observed seven hyperfine lines at 77 K, which exhibits a week interaction in the Cu(II)—Gd(III) core. This data deserves further investigations in order to authenticate this hypothesis and we are at present found difficult to obtain *J* value by magnetic measurements and single crystal e.p.r. study.

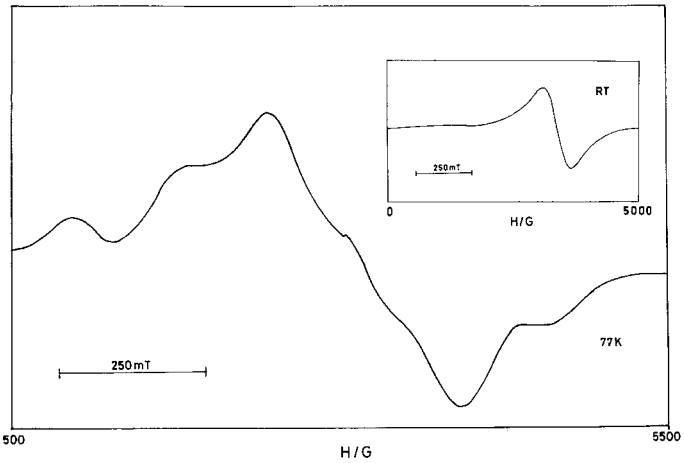


Fig. 3. E.p.r. spectrum of *(2)* in solid state at RT (inserted one) and 77 K; frequency = 9.4023 GHz.

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Supplementary material

Complementary data for the titled compound are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 176083 respectively (e-mail: deposit@ccdc.cam.ac.uk).

References

1. (a) O. Kahn, *Struct. Bonding* (Berlin) **68**, 89 (1987); (b) M. Tadakoro, H. Sakiyama, N. Matsumoto, M. Kodera, H. Okawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 313 (1992).
2. Q.Y. Chen, Q.-H. Luo, L.-M. Zheng, Z.-L. Wang and J.-T. Chen, *Inorg. Chem.*, **41**, 605 (2002).
3. A.D. Watson, S.M. Rocklage and M.J. Carvlin, in *Magnetic Resonance Imaging*, 2nd edit D.D. Stark and W.G. Bradley, (Eds) Mosby Year Book, St Louis, MO, 1992, Vol. 1, pp. 372–437.
4. J.R. Marrow and K.O.A. Chin, *Inorg. Chem.*, **32**, 3357 (1993).
5. H.J. Weinman, R.C. Brach, W.R. Press and G.E. Wesbey, *Am. J. Roentgenol*, **42**, 619 (1984).
6. S.J. Graber, C.M. Harris and E.J. Sinn, *Nucl. Chem.*, **30**, 1805 (1968).
7. A. Bencini, C. Benelli, A. Caneshi, R.L. Carlin, A. Dei and D. Gatteschi, *Inorg. Chem.*, **107**, 8128 (1985).
8. J.P. Costes, A. Dupuis and J.P. Laurent, *J. Chem. Soc., Dalton Trans.*, 735 (1998).
9. J.P. Costes, J.M.C. Juan, F. Dahan, F. Dumestre and J.P. Tuchagues, *Inorg. Chem.*, **41**, 2886 (2002)
10. J.P.Costes, F. Dahan, A. Dupuis and J.P. Laurent, *Inorg. Chem.*, **36**, 3429 (1997).
11. A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, **25**, 572 (1986).
12. O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis and M. Boubekeur, *Inorg. Chem.*, **31**, 110 (1992).
13. T.-H. Lu, H.-H. Yao, J.-M. Lo and S.-F. Tung, *Acta Cryst.*, **C54**, 1600 (1998).
14. E.N. Baker, D. Hall and T.N. Waters, *J. Chem. Soc.*, 400 (1970).
15. E.N. Baker, D. Hall and T.N. Waters, *J. Chem. Soc.*, 406 (1970).
16. H.-H. Yao, B.-H. Chen, J.-M. Lo and F.-L. Laio, *Acta Cryst.*, **C53**, 1222 (1997).
17. I. Ramade, O. Kahn, Y. Jeannin and F. Robert, *Inorg. Chem.*, **36**, 930 (1997).
18. J.P. Costes, F. Dahan, A. Dupuis and J.P. Laurent, *Inorg.Chem.*, **35**, 2400 (1996).
19. M. Sasaki, M. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohha and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 259 (2000).
20. M.L. Kahn, T.M. Rajendiran, Y. Jeannin, C. Mathoniere and O. Kahn, *C.R. Acad. Sci. Paris, Serie IIC, Chime*, **3**, 131 (2000).
21. J.P. Costes, A. Dupuis and J.P. Laurent, *New J. Chem.*, 735 (1999).
22. J.P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
23. S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray and R. Robson, *Chem. Commun.*, 439 (1998).
24. S. Mohanta, H.-H. Lin, C.-J. Lee and H.-H. Wei, *Inorg. Chem., Commun.*, **5**, 585 (2002).
25. A.M. Atria, Y. Moreno, E. Spodine, M.T. Garland and R. Baggio, *Inorg. Chimica Acta*, **335**, 1 (2002).
26. A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems, Springer-Verlag Berlin Heidelberg*, 1990.
27. C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, **29**, 1750 (1990).
28. C.-D. Wu, C.-Z. Lu, J.-C. Liu, H.-H. Zhuang and J.-S. Huang, *J. Chem. Soc., Dalton Trans.*, 3202 (2001).
29. F.M. Ramirez, L. Charbonniere, G. Muller, R. Scopelliti and J.C. Bunzli, *J. Chem. Soc., Dalton Trans.*, 3205 (2001).
30. E.M. Stephens, J.-C.G. Bunzli and G.R. Choppin (Eds) in *Lanthanide Probes in Life, Chemical and Earth Science, Theory and Practice*, Elsevier Science Publications B.V., Amsterdam, 1989 Ch. 6, pp. 181–217.
31. J.A. McMillan, *Electron Paramagnetism*, Reinhold Book Company, New York, 1967.