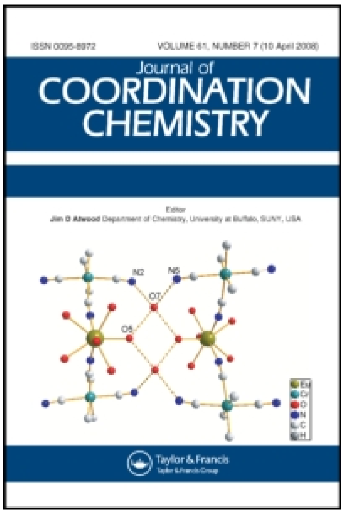
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A novel water soluble 4f-3d heterometallic cyano-bridged complex, $Sm(bipyO_2)_2(H_2O)_2Fe(CN)_6\cdot 4H_2O$

Bing Yan[a]; Yishan Song[a]
[a] Department of Chemistry, Tongji University, Shanghai 200092, China

To cite this Article Yan, Bing and Song, Yishan(2004) 'A novel water soluble 4f-3d heterometallic cyano-bridged complex, $Sm(bipyO_2)_2(H_2O)_2Fe(CN)_6\cdot 4H_2O$', Journal of Coordination Chemistry, 57: 1, 49 — 54
To link to this Article: DOI: 10.1080/00958970310001650050
URL: http://dx.doi.org/10.1080/00958970310001650050

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., Vol. 57, No. 1, 10 January 2004, pp. 49–54

Taylor & Francis
Taylor & Francis Group

A NOVEL WATER SOLUBLE 4f–3d HETEROMETALLIC CYANO-BRIDGED COMPLEX, $Sm(bipyO_2)_2(H_2O)_2Fe(CN)_6 \cdot 4H_2O$

BING YAN* and YISHAN SONG

Department of Chemistry, Tongji University, Shanghai 200092, China

(Received in final form 26 September 2003)

Reaction of 2,2′-bipyridine-*N*,*N*′-dioxide ($bipyO_2$) with $Sm(NO_3)_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$ affords a novel cyano-bridged complex $Sm(bipyO_2)_2(H_2O)_2Fe(CN)_6 \cdot 4H_2O$ (SmFe). The title complex crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters $a = 10.3230(14)$, $b = 12.5102(18)$, $c = 13.8996(19)$ Å, $\alpha = 85.273(2)$, $\beta = 88.170(2)$, $\gamma = 70.525(2)°$, its single-crystal X-ray structure refined to $R_1 = 0.0371$, $wR_2 = 0.0772$. The luminescence of SmFe quenches more easily than binary samarium complex with $bipyO_2$.

Keywords: Cyano-bridged; 4f–3d Complex; Crystal structure; Samarium hexacyanoferrate; 2,2′-Bipyridine-*N*,*N*′-dioxide

INTRODUCTION

Molecular-based magnetic materials represents an active research area [1–3] and cyano-bridged complexes (Prussian blue analogues) are a class of important molecular-based magnets [4–6]. Extensive research has been carried out on the structures and magnetic properties of cyano-bridged complexes, mainly focused on transition metal cyano-bridged complexes [7–9]. Recently a series of zero-dimensional (dinuclear, trinuclear), one-dimensional chain, two-dimensional layer and hydrogen-bonded ion pair 4f–3d complexes using 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-bipyridyl-*N*,*N*′-dioxide, *N*,*N*′-dimethylformide, bipymidine, *N*,*N*′-dimethylformide, *N*,*N*′-dimethylacetamide as hybrid ligands [10–22] have been reported. It can be seen that the hybrid ligands, rare earth ions and transition metal ions influence the composition, the coordination environment of rare earth ions and the crystal structure. Steric effects of hybrid ligands have great influences on the coordination environment of rare earth ions and the crystal structures of complexes. For example, with 2-pyrrolidinone, dinuclear cyano-bridged complexes form $[Ln(pyo)_4(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ ($Ln = Ce \sim Er$), $Ln(pyo)_5(H_2O)_2Cr(CN)_6 \cdot 2pyo \cdot 2H_2O$ ($Ln = Ce \sim Nd$) and $Ln(pyo)_5(H_2O)_3Fe(CN)_6 \cdot 2H_2O$ ($Ln = Sm \sim Er$)]; with *N*-methylpyrrolidinone, ion-pair complexes form

---

*Corresponding author. Fax: +86-21-65984663. E-mail: byan@tongji.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001650050

$[Ln(MPL)_3(H_2O)_5Fe(CN)_6$ $(Ln = La \sim Dy)]$ because the methyl group in the MPL molecule enhances steric hindrance; with 1,8-napthanthroline, 1,10-phenanthroline, 2,2′-bipyridine, 2,2′:6′2′-tetrapyridine and betaine as hybrid ligands, one-dimensional chain complexes are obtained [19,20]; with bipyrimidine, two-dimensional layer-like compounds are formed. In addition, we have prepared ion-pair complexes with different terminal ligands using $Er(NO_3)_5$ and $Fe(CN)_6$. The coordination environment of the Er ion may be different; for *N*-pyrrolidinone, four MPL ligands surround the Er ion; for *N*,*N*′-dimethylacetamide, only three DMA ligands do so [22]. Using different $[M(CN)_6]^{3-}$ (M = transition metal) molecular fragments as building blocks, one can obtain different coordination of rare earth ions and crystal structures of complexes. In the present work, we employed 2,2′-bipyridine-*N*,*N*′-dioxide ($bipyO_2$) as a hybrid terminal ligand to synthesize a novel water soluble cyano-bridged complex, $Sm(bipyO_2)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$. Its crystal structure and luminescence properties are discussed below.

EXPERIMENTAL

Materials and Methods

$Sm(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving samarium oxide in concentrated nitric acid and drying. The ligand 2,2′-bipyridine-*N*,*N*′-dioxide ($bipyO_2$) was synthesized according to the literature [23]. Other reagents were commercially available and used without further purification. Elemental analyses (C, H, N) were carried out using an Elementar Cario EL instrument. Infrared spectroscopy using KBr pellets was performed on a Nicolet 7199B spectrophotometer in the 4000–400 cm^{-1} range. Excitation and emission spectra were measured with a Perkin-Elmer LS-55 spectrophotometer.

Synthesis of $Sm(bipyO_2)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$

To a mixed aqueous solution of $Sm(NO_3)_3 \cdot 6H_2O$ and 2,2′-bipyridine-*N*,*N*′-dioxide ($bipyO_2$) was added an equimolar amount of $K_3[Fe(CN)_6]$ in a minimum amount of water. The resulting yellow solution was kept undisturbed in the dark. After about some hours, well-shaped, light-yellow crystals were obtained. Anal. Calcd. for $C_{26}H_{30}SmFeN_{10}O_{11}$(%): C, 36.11; H, 3.50; N, 16.20. Found: C, 35.89; H, 3.28; N, 16.07. IR: $\nu_{s\,O\text{–}H}$ (3418 cm^{-1}), $\nu_{s\,CN}$ (2121 cm^{-1}, 2143 cm^{-1}), $\nu_{s\,C\text{–}O}$ (1652 cm^{-1}, 1671 cm^{-1}).

X-ray Crystallography

X-ray diffraction data for a crystal with dimensions 0.05 × 0.10 × 0.20 mm were collected with graphite-monochromated Mo Ka radiation on an Enraf-Nonius CAD4 four-circle diffractometer. Data were collected by the ω–2θ scan technique. The crystal structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ where $w = [s^2(F_o^2) + (0.0727\,P)^2 + 0.0000\,P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were added geometrically and not refined. All calculations were performed using the programs SHELXS-97 and SHELXL-97 [24,25]. A summary of crystallographic data and refinement parameters is given in Table I.

TABLE I Crystal data and structure refinement for the title complex

Complex	$Sm(bipyO_2)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$
Formula	$C_{26}H_{30}FeSmN_{10}O_{11}$
Relative molecular weight M	864.80
Colour	Yellow
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	Mo Kα
Crystal system	$P\bar{1}$
Space group	Triclinic
Unit dimensions	$a = 10.3230(14)$ Å $b = 12.5102(18)$ Å $c = 13.8996(19)$ Å $\alpha = 85.273(2)°$ $\beta = 88.170(2)°$ $\gamma = 70.525(2)°$
Volume	1686.6(4) Å^3
Z	2
Calculated density	1.703 Mg/m^3
Absorption coefficient	2.225 mm^{-1}
$F(000)$	864
Crystal size	$0.05 \times 0.10 \times 0.20$ mm
θ range for data collection	1.47° to 27.01°
Reflections/collected/unique	8472/7130 [R(int) = 0.0227]
Completeness to $2\theta = 25.01$	96.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7130/0/442
Goodness-of-fit on F^2	0.948
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0371$, $wR2 = 0.0771$
Largest diff. peak and hole	0.950 and -0.752 e Å^{-3}

Additional material is available from the Cambridge Crystallographic Data Centre, No: CCDC-215780.

RESULTS AND DISCUSSION

Final atomic coordinates for non-hydrogen atoms are listed in Table II. Figure 1 shows an ORTEP drawing of the SmFe complex. Samarium is coordinated by seven oxygen atoms from two $bipyO_2$ molecules and three water molecules, and a nitrogen atom from the bridging CN group. The geometry of the samarium ion can be described as a distorted 4,4-bicapped trigonal prism. The bond distance between Sm^{3+} and the bridging nitrogen atom is 2.442(4) Å [Sm–N(1)]. Bond distances between Sm and the O atoms from H_2O molecules ranges from 2.421(3) to 2.442(3) Å and range from 2.339(3) to 2.444(4) Å between Sm and O atoms of $bipyO_2$ molecules. Four uncoordinated water molecules are present in the unit cell.

The geometry of the $Fe(CN)_6^{3-}$ ion is approximately octahedral with coordination of six CN ligands. The Fe–C bond distances range from 1.927(5) to 1.947(5) Å and the bridging Fe(1)–C(1) distance is 1.993(6). Bond angles Fe–C–N range from 176.7(4) to 179.9(7)°. Although the Fe–C and C≡N distances vary, they are all normal. Fe–C–N bond angles do not significantly deviate from linearity. However, the bridging CN ligand is coordinated to the Sm atom in a bent mode, which may be due to the effect of steric hindrance of the coordinated $bipyO_2$ molecules around the Sm atom. Table III gives the selected bond lengths and angles data.

TABLE II Final atomic coordinates and $10^3\,Å^2$ of equivalent isotropic displacement parameters for the title complex

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Sm(1)	9657(1)	7904(1)	2245(1)	24(1)
Fe(1)	5845(1)	12 232(1)	2091(1)	29(1)
O(1)	11 321(3)	8865(3)	2474(2)	35(1)
O(2)	10 611(3)	7392(3)	3815(2)	39(1)
O(3)	9493(3)	6020(2)	2564(2)	31(1)
O(4)	8291(3)	7635(3)	1039(2)	34(1)
O(5)	10 006(3)	8877(3)	714(2)	40(1)
O(6)	11 682(3)	6670(2)	1479(2)	32(1)
O(7)	7739(3)	7938(3)	3330(2)	45(1)
N(1)	11 348(4)	9410(3)	3255(3)	34(1)
N(2)	11 970(4)	6925(3)	3892(3)	39(1)
N(3)	9579(4)	5266(3)	1929(3)	31(1)
N(4)	7148(4)	7401(3)	1273(3)	34(1)
C(1)	10 720(5)	10 540(4)	3246(4)	48(1)
C(2)	10 785(6)	11 109(5)	4013(5)	62(2)
C(3)	11 477(6)	10 541(5)	4812(4)	59(2)
C(4)	12 103(5)	9398(5)	4834(4)	49(1)
C(5)	12 029(4)	8815(4)	4046(3)	35(1)
C(6)	12 743(5)	7593(4)	4003(3)	37(1)
C(7)	14 145(5)	7102(5)	4082(3)	50(1)
C(8)	14 751(6)	5957(5)	4026(4)	61(2)
C(9)	13 954(7)	5312(5)	3922(4)	69(2)
C(10)	12 542(6)	5799(4)	3860(3)	56(2)
C(11)	10 729(5)	4358(4)	1914(3)	41(1)
C(12)	10 850(5)	3538(4)	1292(4)	53(1)
C(13)	9776(6)	3618(5)	702(4)	59(2)
C(14)	8608(5)	4542(4)	738(4)	49(1)
C(15)	8504(5)	5377(4)	1356(3)	34(1)
C(16)	7196(5)	6311(4)	1443(3)	32(1)
C(17)	5988(5)	6095(5)	1658(3)	46(1)
C(18)	4772(5)	6986(5)	1709(4)	57(2)
C(19)	4763(5)	8061(5)	1534(4)	61(2)
C(20)	5958(5)	8271(5)	1303(4)	49(1)
N(5)	8085(4)	9891(3)	2404(3)	44(1)
N(6)	3660(4)	14 582(3)	1670(3)	50(1)
N(7)	7308(4)	12 477(4)	168(3)	55(1)
N(8)	4028(5)	11 089(4)	1152(3)	59(1)
N(9)	4368(5)	11 947(5)	4000(3)	71(2)
N(10)	7585(5)	13 321(4)	3179(4)	72(2)
C(21)	7249(4)	10 760(4)	2317(3)	33(1)
C(22)	4474(5)	13 705(4)	1817(3)	35(1)
C(23)	6761(5)	12 391(4)	885(3)	36(1)
C(24)	4710(5)	11 516(4)	1478(3)	36(1)
C(25)	4910(5)	12 053(4)	3297(4)	40(1)
C(26)	6951(5)	12 917(4)	2765(4)	43(1)
O(8)	1977(4)	3422(3)	5021(3)	67(1)
O(9)	601(4)	5792(3)	5886(3)	68(1)
O(10)	8415(7)	9451(6)	9124(5)	53(3)
O(11)	7800(8)	9965(7)	9622(6)	55(3)
O(13)	4927(11)	9513(9)	3377(9)	58(4)
O(12)	5378(7)	9330(6)	4033(6)	77(3)

In the unit cell there are two types of hydrogen bonding; one is intra-chain hydrogen bonding between a coordinated water molecule in a complex unit and a CN of another. The second is inter-chain hydrogen bonding involving a lattice water molecule. The O atom of an uncoordinated water molecule forms a hydrogen bond with an H atom

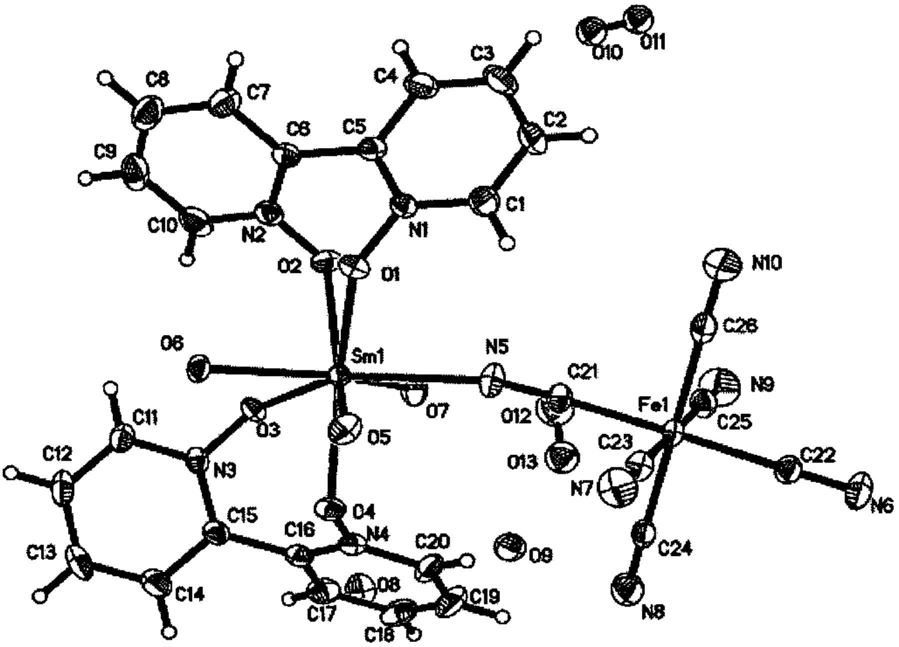


FIGURE 1 ORTEP drawing of $Sm(bipyO_2)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$.

TABLE III Selected bond lengths (Å) and bond angle (°) for the title complex

Sm(1)–O(4)	2.339(3)	Fe(1)–C(21)	1.935(5)
Sm(1)–O(2)	2.372(3)	Fe(1)–C(26)	1.942(5)
Sm(1)–O(6)	2.421(3)	Fe(1)–C(25)	1.942(5)
Sm(1)–O(3)	2.423(3)	Fe(1)–C(24)	1.947(5)
Sm(1)–O(5)	2.441(3)	N(5)–C(21)	1.141(5)
Sm(1)–O(7)	2.442(3)	N(6)–C(22)	1.145(5)
Sm(1)–O(1)	2.444(3)	N(7)–C(23)	1.145(5)
Sm(1)–N(5)	2.498(4)	N(8)–C(24)	1.139(6)
Fe(1)–C(23)	1.927(5)	N(9)–C(25)	1.131(6)
Fe(1)–C(22)	1.930(5)	N(10)–C(26)	1.143(6)
O(4)–Sm(1)–O(2)	149.12(11)	O(1)–Sm(1)–N(5)	79.33(12)
O(4)–Sm(1)–O(6)	89.75(10)	C(23)–Fe(1)–C(22)	90.66(19)
O(2)–Sm(1)–O(6)	93.37(10)	C(23)–Fe(1)–C(21)	87.17(19)
O(4)–Sm(1)–O(3)	72.35(10)	C(22)–Fe(1)–C(21)	177.83(19)
O(2)–Sm(1)–O(3)	78.68(10)	C(23)–Fe(1)–C(26)	91.7(2)
O(6)–Sm(1)–O(3)	75.75(10)	C(22)–Fe(1)–C(26)	90.6(2)
O(4)–Sm(1)–O(5)	69.45(10)	C(21)–Fe(1)–C(26)	89.7(2)
O(2)–Sm(1)–O(5)	140.34(11)	C(23)–Fe(1)–C(25)	179.0(2)
O(6)–Sm(1)–O(5)	72.17(10)	C(22)–Fe(1)–C(25)	89.63(19)
O(3)–Sm(1)–O(5)	129.37(10)	C(21)–Fe(1)–C(25)	92.53(19)
O(4)–Sm(1)–O(7)	85.56(11)	C(26)–Fe(1)–C(25)	89.3(2)
O(2)–Sm(1)–O(7)	74.07(11)	C(23)–Fe(1)–C(24)	91.1(2)
O(6)–Sm(1)–O(7)	144.09(11)	C(22)–Fe(1)–C(24)	90.23(19)
O(3)–Sm(1)–O(7)	68.89(10)	C(21)–Fe(1)–C(24)	89.62(19)
O(5)–Sm(1)–O(7)	137.23(11)	C(26)–Fe(1)–C(24)	177.1(2)
O(4)–Sm(1)–O(1)	140.32(10)	C(25)–Fe(1)–C(24)	87.9(2)
O(2)–Sm(1)–O(1)	70.11(10)	N(1)–O(1)–Sm(1)	123.5(2)
O(6)–Sm(1)–O(1)	78.64(10)	N(2)–O(2)–Sm(1)	118.1(2)

(*Continued*)

TABLE III Continued

O(3)–Sm(1)–O(1)	137.96(10)	N(3)–O(3)–Sm(1)	127.3(2)
O(5)–Sm(1)–O(1)	70.87(10)	N(4)–O(4)–Sm(1)	120.2(2)
O(7)–Sm(1)–O(1)	125.05(10)	C(21)–N(5)–Sm(1)	166.3(4)
O(4)–Sm(1)–N(5)	91.76(12)	N(5)–C(21)–Fe(1)	176.7(4)
O(2)–Sm(1)–N(5)	101.82(12)	N(6)–C(22)–Fe(1)	178.9(5)
O(6)–Sm(1)–N(5)	147.03(12)	N(7)–C(23)–Fe(1)	179.5(4)
O(3)–Sm(1)–N(5)	135.66(11)	N(8)–C(24)–Fe(1)	177.5(5)
O(5)–Sm(1)–N(5)	77.59(12)	N(9)–C(25)–Fe(1)	179.9(7)
O(7)–Sm(1)–N(5)	68.81(12)	N(10)–C(26)–Fe(1)	178.6(5)

of a coordinated water molecule while the H atom of a lattice water molecule forms another hydrogen bond with a terminal CN group.

The emission spectrum of $Sm(bipyO_2)_2(NO_3)_3 \cdot 2H_2O$ with excitation at 242 nm, gives three emission bands at 562.5, 603.5 and 643.0 nm are observed. The emission spectrum of $Sm(bipyO_2)_2(H_2O)_3Fe(CN)_6 \cdot 4H_2O$ shows three similar emission bands with peaks at 558.5, 598.0 and 643.5 nm, but with much lower luminescence intensities. These correspond with the characteristic emission $^4G_{5/2} \rightarrow {}^6H_j$ ($j = 5/2, 7/2, 9/2$) transitions of the Sm^{3+} ion. The weak luminescence of cyano-bridged complex is caused by the cyano group between the Sm ion and Fe ion, which quenches emission originating from intramolecular energy transfer from 2,2′-bipyridine-*N*,*N*-dioxide.

References

[1] O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science* **271**, 49 (1996).

[2] O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science* **272**, 704 (1996).

[3] D.G. Fu, J. Chen, X.S. Tan, L. Jiang, S.W. Zhang, P.J. Zheng and W.X. Tang, *Inorg. Chem* **36**, 220 (1997).

[4] M. Ohba, H. Okawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.* **119**, 1011 (1997).

[5] H.Z. Kou, S. Gao, J.G.H. Zhang, G. Su, R.K. Zheng and X.X. Zhang, *J. Am. Chem. Soc.* **123**, 11809 (2001).

[6] H.Z. Kou, J.K. Tang, D.Z. Liao, S. Gao, P. Cheng, Z.H. Jiang, S.P. Yan, G.L. Wang, B. Chansou and J.P. Tuchagues, *Inorg. Chem.* **40**, 4839 (2001).

[7] H.Z. Kou, S. Gao, B.Q. Ma and D.Z. Liao, *Chem. Commun.* 1309 (2000).

[8] H.Z. Kou, S. Gao, B.Q. Ma and D.Z. Liao, *Chem. Commun.* 713 (2000).

[9] X.M. Chen, M.L. Tong, Y.L. Wu, Y.Y. Yang, S.M.J. Aubin and D.N. Hendrickson, *Inorg. Chem.* **37**, 6186 (1998).

[10] J.P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.* **39**, 165 (2000).

[11] J.P. Costes, F. Dahan, A. Dupuis and J.P. Laurent, *Inorg. Chem.* **39**, 169 (2000).

[12] Q.D. Liu, S. Gao, J.R. Li, Q.Z. Zhou, K.B. Yu, B.Q. Ma, S.W. Zhang, X.X. Zhang and T.Z. Jin, *Inorg. Chem.* **39**, 2488 (2000).

[13] H.Z. Kou, S. Gao, B.W. Sun and J. Zhang, *Chem. Mater.* **13**, 1431 (2001).

[14] B. Yan, Z.D. Chen, S.X. Wang and S. Gao, *Chem. Lett.* 354 (2001).

[15] J.P. Liu, E.A. Meyers, J.A. Cowan and S.G. Shore, *Chem. Commun.* 2043 (1998).

[16] D.W. Knoeppel, J.P. Liu, E.A. Meyers and S.G. Shore, *Inorg. Chem.* **37**, 4828 (1998).

[17] B. Du, E.A. Meyers and S.G. Shore, *Inorg. Chem.* **39**, 4639 (2000).

[18] B. Yan, H.D. Wang and Z.D. Chen, *Polyhedron* **20**, 591 (2001).

[19] B. Yan and Z.D. Chen, *Helv. Chim. Acta* **84**, 817 (2001).

[20] H.Z. Kou, S. Gao and X.L. Jin, *Inorg. Chem.* **40**, 6295 (2001).

[21] H.Z. Kou, S. Gao, C.H. Li, D.Z. Liao, B.C. Zhou, R.J. Wang and Y.D. Li, *Inorg. Chem.* **41**, 6887 (2002).

[22] K.R. Sun, Z.D. Chen, F. Yan, S. Gao, K.K. Cheung, C.M. Che and X.X. Zhang, *J. Cluster Sci.* **13**, 103 (2001).

[23] P.G. Simopson, A. Vinciguerre and J.V. Quagliano, *Inorg. Chem.* **2**, 282 (1963).

[24] G.M. Sheldrick, *Acta Cryst.* **A46**, 467 (1990).

[25] G.M. Sheldrick, SHELXS-97, A Program for X-Ray Crystal Structure Solution, and SHELXL-97, A Program for X-ray Structure Refinement (Göttingen University, Germany, 1997).