ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 1046–1051

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Synthesis and X-ray crystal structure of cationic polynuclear hydroxide acetylacetonate lanthanide(III) clusters with homodinuclear or heterodinuclear decacarbonyl hydrides: $[HMo_2(CO)_{10}]^-$ and $[HCrW(CO)_{10}]^-$

M. Volpe [a,*], G. Bombieri [b], N. Marchini [b]

[a] *Department of Chemical Engineering of Processes and Materials, University of Palermo, 90128 Palermo, Italy*
[b] *Institute of Pharmaceutical Chemistry, University of Milano, 20131 Milano, Italy*

Received 23 July 2004; received in revised form 1 December 2004; accepted 2 December 2004

Abstract

The synthesis and characterization of new polynuclear lanthanide(III) ionic clusters of general formula $[Ln_9(acac)_{16}(OH)_{10}]^+$ $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ (Ln = Sm, Eu, Gd, Dy, Yb) and $[Sm_9(acac)_{16}(OH)_{10}]^+$ $[CrW(CO)_{10}(\mu\text{-}H)]^-$ is reported. The polynuclear complexes, prepared under pure nitrogen atmosphere by interaction of the hydridic metal carbonyls with the β-dichetonate $Ln(acac)_3{\cdot}3H_2O$ (Ln = Sm, Eu, Gd, Dy, Yb). The new clusters were characterized by elemental analysis, complexometric titration for Ln, atomic absorption for Cr, W and Mo, gas-volumetric analysis for CO, FTIR spectroscopy and single crystal X-ray structure determination of $[Sm_9(acac)_{16}(OH)_{10}][Mo_2(CO)_{10}(\mu\text{-}H)]$. The Eu and Yb complexes are isostructural to the Sm one for which, similarly to their homonuclear chromium and tungsten derivative analogues, a square antiprismatic arrangement of eight Sm ions with the ninth at the center of the antiprism has been found.

Keywords: Lanthanides; Metal carbonyls; Clusters; Crystal structure

1. Introduction

Mixed 3d–4f metal complexes showed magnetic, optical and catalytic activities mainly due to their electronic properties that increased the interest for this type of complexes [1–4]. Although heteronuclear complexes containing 3d and 4f metals are believed to lead to extraordinary physico-chemical properties, the lack of rational synthesis of such species is the reason of their limited studies [5–7]. A series of trinuclear Cu(II)Ln(III)Cu(II) complexes with 2,6-di(acetoacetyl)pyridine "due to its potential selection of different metals" has been recently prepared [5]. The complexes obtained have different magnetic properties depending on the presence of the different lanthanide species due to their different interaction with the terminal coppers. Variations in the cluster metal composition can be made for a tunable behavior of their physico-chemical properties as for example luminescence lifetimes for terbium(III) and europium(III) nanoclusters [8], electron relaxation devices for the gadolinium nanoclusters in magnetic resonance imaging applications [9,10].

Recently, heteronuclear compounds, obtained by reaction of lanthanide complexes with transition metal carbonyls, were used in selective catalytic processes [11].

Organo-lanthanide cations (Ln = Sm or Yb) and $[Co(CO)_4]^-$ as counter anion, have also been isolated and characterized [12,13]. A variety of lanthanide clusters have been obtained as tetra [14,15], penta [16], hexa [15b,e,17] octa [18], nona [19], dodeca [15b,e], tetradeca [20] and pentadecanuclear [15b] derivatives generally controlling the hydrolysis of the metal ion salts but some time for

---

[*] Corresponding author. Tel.: +39 091 6567232; fax: +39 091 6567280.
E-mail address: volpe@dicpm.unipa.it (M. Volpe).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.132

serendipity. In the case of heptanuclear hydroxo cluster $[Ln_7(\mu_3OH)_8]^{13+}$ [21], the synthesis was made by hydrothermal reaction with the aid of 1,4-naphtalene dicarboxylate (1,4-NDA) that give rise to porous lanthanide polymers having a dicubane like structure of the hydroxo core that is a frequent structural motif in lanthanide hydroxo clusters. As part of our program of developing new polynuclear lanthanide oxo-cluster compounds containing transition metals [22–24] we report the synthesis and spectroscopic characterization of $Sm_9(acac)_{16}(OH)_{10}[CrW(CO)_{10}(\mu\text{-}H)]$ and of the compounds having general formula $Ln_9(acac)_{16}(OH)_{10}[Mo_2(CO)_{10}(\mu\text{-}H)]$ (Ln = Sm, Eu, Gd, Dy, Yb). These new ionic clusters were isolated by reaction of binuclear hydridic carbonyls $[CrW(CO)_{10}(\mu\text{-}H)]^-$ with $Sm(acac)_3{\cdot}3H_2O$ and $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ with tris-2,4-pentanedionates, $Ln(acac)_3{\cdot}3H_2O$ (Ln = Sm Eu, Gd, Dy, Yb).

2. Experimental

Due to the high sensitivity of metal carbonyls to oxygen all the interactions and the treatments involving the reactants and the products were carried out under pure nitrogen atmosphere by using standard nitrogen-vacuum technique. The 2,4-pentanedionate complexes $Ln(acac)_3{\cdot}3H_2O$ (Ln = Dy, Gd, Sm) were reagent grade and purchased either by Aldrich or Strem Chemicals. Ytterbium and europium derivatives were prepared in our laboratories by a convenient route as reported in literature [25]. The homo-nuclear hydridic carbonyl $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ and the mixed metal carbonyl $[CrW(CO)_{10}(\mu\text{-}H)]^-$ were synthesized by modifying a published procedure obtaining shorter times of reaction and higher yields in the products. The hetero-bimetallic chromium–tungsten compound was isolated by 4-h reaction of $W(CO)_6$ (5 mmol) with a freshly prepared warm (48 °C) THF/methanol (5/1, v/v) mixture containing as unique carbonyl species $HCr(CO)_5{}^-$ (FTIR and ^{1}H NMR evidence). The mononuclear species was prepared by 1.5-h reaction of 5 mmol of $Cr(CO)_6$ with 35 mmol of KOH dissolved in the above mentioned solvent mixture. The main isolated product $KCrW(CO)_{10}(\mu\text{-}H)$ contains small amounts of $KCr_2(CO)_{10}(\mu\text{-}H)$ species removed by treatment with Et_2O/CH_2Cl_2 mixture (1/2, v/v) in which the latter is more soluble than the former. Higher yields in $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ (ca. 55%) were achieved by removing water from the solvents reaction mixture and by using a 5/1 (v/v) THF/methanol solvent ratio. The water elimination and a low methanol content drastically reduce the formation of the hydroxide byproduct $K_3Mo_2(OH)_3(CO)_6$ obtained in large amount, following the procedure previously quoted. The products were characterized by complexometric titration with standardized (0.0101 M) EDTA solution, using xylenol orange as indicator for lanthanides [25], back titration with standardized $Zn(NO_3)_2$ solution (0.01 M) using PAR as indicator for Cr, Mo and W. Atomic absorption spectroscopy for Cr, Mo and W was carried out on a Varian AA 100 Plus and gas-volumetric analysis of CO in samples decomposed by iodine in EtOH solutions. IR absorption spectra were recorded on a Shimadtzu 8400 FTIR spectrometer using nujol mulls on KBr windows or KBr pellets for sample in solid state and NaCl rectangular windows for samples dissolved in solution. ^{1}H NMR spectra were recorded on a Bruker AMX 300 spectrometer. Elemental analyses were carried out on a Fisons Instruments EA 1108 elemental analyzer.

Reaction of potassium salt adducts of $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ and $[CrW(CO)_{10}(\mu\text{-}H)]^-$ with $Ln(acac)_3{\cdot}3H_2O$ (Ln = Sm, Eu, Gd, Dy and Yb) yielded, respectively, a series of new ionic clusters: $[Ln_9(acac)_{16}(OH)_{10}][Mo_2(CO)_{10}(\mu\text{-}H)]$ (Ln = Sm, Eu, Gd, Dy, Yb) (**1a–e**) and $[Sm_9(acac)_{16}(OH)_{10}][CrW(CO)_{10}(\mu\text{-}H)]$ (**2a**).

Different reaction conditions were fully investigated in order to get best yields in the main products. The influence of various reaction conditions was investigated. Molar ratios of reactants between 1:1 and 2:1, in EtOH, THF or Me_2CO as solvents, with temperature range from 25 to 50 °C and time of reaction not longer than 2 h gave the best results. In particular, the use of ethanol as solvent leads to higher yields in the main products.

*2.1. Synthesis of complexes: $[HMo_2(CO)_{10}][Ln_9(OH)_{10}(acac)_{16}]$(**1a–e**) and $[HCrW(CO)_{10}][Sm_9(OH)_{10}(acac)_{16}]$(**2a**)*

1a–e: $Ln(acac)_3{\cdot}3H_2O$ (Ln = Sm, Eu, Gd, Dy, Yb) (1 mmol) was slowly dissolved in EtOH (30 mL) previously carefully deareated and nitrogen (99.999%) saturated by three freeze–pump–thaw cycles. To the clear stirred solution, gradually warmed to 48 °C (±1 °C), was slowly added (drop by drop) a pale yellow ethanol solution (30 mL) of $K[Mo_2(CO)_{10}(\mu\text{-}H)]$ (1.02 g, 2 mmol).

From the resulting solution, a white crystalline solid soon separated. The mixture was left to stir at 48 °C (±1 °C) for 2 h, then to cool at room temperature and filtered off. The white crystalline products **1a–e**, collected by filtration, were purified with several ethanol washes in which any unreacted $K[HMo_2(CO)_{10}]$ or $Ln(acac)_3{\cdot}3H_2O$ are very soluble, and well dried under vacuum. Usual yields, based on Ln, up to 75% (**1a** 75%, **1b** 60%, **1c** 70%, **1d** 72%, **1e** 55%). They were recrystallized (ca. 70% yield) at room temperature under nitrogen for at least 5 days, by slowly diffusing toluene in a chloroform solution of **1** (ca. 0.15 mmol in 30 ml) 1:1 (v/v) $CHCl_3$/toluene. The products **1a–e** are soluble in CH_2Cl_2, $CHCl_3$, THF and Me_2CO, slightly soluble in MeOH, insoluble in EtOH, toluene, Et_2O and water. Well-dried, solid samples of **1** are not stable in air and slowly decompose giving molybdenum hexacarbonyl solutions which are air sensitive. The products can be stored for few months if well sealed under nitrogen at low temperatures. Table 1 shows analytical data for the isolated complexes. **2a** was synthesized by a procedure similar to that above reported. In particular, interaction between $Sn(acac)_3{\cdot}3H_2O$ and $K[HCrW(CO)_{10}]$ was carried out for 3 h at 50 °C (78% yield).

Table 1
Analytical results of the complexes $Ln_9(acac)_{16}(OH)_{10}[Mo_2(CO)_{10}(\mu\text{-}H)]$ and $Sm_9(acac)_{16}(OH)_{10}[CrW(CO)_{10}(\mu\text{-}H)]$

Complex	% of Ln found (calculated)	% of C found (calculated)	% of H found (calculated)	% of CO found (calculated)	% of Mo found (calculated)	% of Cr found (calculated)	% of W found (calculated)
$[HMo_2(CO)_{10}][Sm_9(OH)_{10}(acac)_{16}]$ **(1a)**	37.75 (37.78)	30.12 (30.18)	3.48 (3.46)	7.78 (7.82)	5.32 (5.37)	–	–
$[HMo_2(CO)_{10}][Eu_9(OH)_{10}(acac)_{16}]$ **(1b)**	37.98 (38.03)	29.98 (30.06)	3.59 (3.45)	7.82 (7.79)	5.26 (5.34)	–	–
$[HMo_2(CO)_{10}][Gd_9(OH)_{10}(acac)_{16}]$ **(1c)**	38.82 (38.84)	29.57 (29.66)	3.54 (3.40)	7.63 (7.69)	5.19 (5.27)	–	–
$[HMo_2(CO)_{10}][Dy_9(OH)_{10}(acac)_{16}]$ **(1d)**	39.57 (39.62)	29.22 (29.28)	3.43 (3.36)	7.55 (7.59)	5.18 (5.20)	–	–
$[HMo_2(CO)_{10}][Yb_9(OH)_{10}(acac)_{16}]$ **(1e)**	41.06 (41.13)	28.52 (28.55)	3.33 (3.27)	7.34 (7.40)	5.00 (5.07)	–	–
$[HCrW(CO)_{10}][Sm_9(OH)_{10}(acac)_{16}]$ **(2a)**	37.28 (37.32)	29.77 (29.81)	3.46 (3.42)	7.69 (7.72)	–	1.39 (1.43)	5.02 (5.07)

Table 2
Crystal data and structure refinement for Sm (**1a**)

Empirical formula	$C_{90}H_{112}Mo_2O_{52}Sm_9$
Formula weight	3570.83
Temperature	293(2) K
Crystal system	Tetragonal
space group	I-4c2(120)
Unit cell dimensions	$a = b$ 21.645(2)Å, $c = 26.307(2)$Å
Volume	12325.1 $Å^3$
Calculated density (Z)	4, 1.924 mg/m^3
Absorption coefficient	4.491 mm^{-1}
$F(0\,0\,0)$	6840
Crystal size	0.15 mm × 0.18 mm × 0.09 mm
θ range for data collection	2.66–23.98°
Limiting ind.	$-1 < h < 24$, $-1 < k < 24$, $-1 < l < 30$
Reflections collected/unique	5769/4820
Completeness to θ	23.98 99.8%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data/rest./param	4820/32/304
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.058$, $wR_2 = 0.15$

3. Structure determination of Sm derivative (1a)

Crystal data and structure refinement are in Table 2. The cell parameters of the isomorphous Eu are $a = b = 21.65(1)$, $c = 26.31(1)$ and for Yb are $a = b = 21.54(1)$, $c = 26.33(1)$.

The intensity data were collected on a CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ, 0.71073 Å). The cell parameters were determined and refined by least-squares fit of 20 high-angle reflections. The structure was solved by Patterson methods and conventional Fourier synthesis (SHELX-86) [26]. The refinement was made by full matrix least-squares on F^2 (SHELX-97) [26]. All non-H-atoms were refined anisotropically. The H-atoms were introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atom with fixed isotropic thermal parameters (1.2 Uequiv. of the parent carbon atom).

Selected bond distances are reported in Table 3. The supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC deposition number 254789). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

4. Results and discussion

4.1. *Crystal structure of (**1a**)*

The crystal structure is shown in Fig. 1 where a view of the complex cation is reported.

Its structure is close to that of the analogous $[M_2(CO)_{10}(\mu\text{-}H)]^-$ derivatives (M = Cr, W). The substitution of chromium or tungsten with molybdenum in the anion do not cause significant variations either in the cluster composition either

Table 3
Selected bond lengths (Å) for (**1a**)

Sm1–Sm2	3.802(1)
Sm1–Sm3	3.778(1)
Sm2–Sm3	3.690(1)
Sm1–O1(ox)	2.464(12)
Sm1–O2(ox)	2.484(13)
Sm2–O1	2.624(4)
Sm3–O1	2.646(9)
Sm2–O2	2.531(14)
Sm2–O3	2.372(19)
Sm2–O4	2.302(15)
Sm2–O5	2.362(18)
Sm2–O7	2.443(15)
Sm2–O2(ox)	2.341(14)
Sm3–O6	2.382(22)
Sm3–O7	2.508(15)
Sm3–O8	2.386(15)
Sm3–O9	2.256(24)
Sm3–O1(ox)	2.380(13)
Sm3–O2(ox)	2.366(14)
Mo1–C1C	1.81(9)
Mo1–C2C	2.02(4)
Mo1–C3C	1.89(4)

in the molecular assembling with the same ratio ligands metal ions in the cationic $Sm_9(acac)_{16}(OH)_{10}$ cluster. Eight Sm atoms are at the vertices of a square antiprism while the ninth is at the center of three perpendicular crystallographic binary axes. The central Sm is connected by hydroxo bridges (μ_3OH) to the other eigth, at distances of 2.46(1) Å with O1(ox) and 2.48(1) Å with O2(ox) with an antiprismatic coordination geometry while the Sm at the vertices are connected either by hydroxo bridges (μ_3OH) (Sm2–O 2.36(1) Å on average) and by bridging acetylacetonate ligands (Eu–O 2.48(1) Å, averaged value). The top and the bottom of the so formed barrel have at the center a hydroxyl moiety bridging (μ_4OH) the four adjacent samariums. The coordination geometry of the periphreral metal ions is rather irregular due to the different origin of the coordinating oxygens (μ_3OH), (μ_4OH) and acetyl acetonate. The latter adopts different coordination modes bridgingbidentate or chelating on the same metal ion. The coordination number of Sm is eigth in any case but for the peripherals no well-defined geometry can be detected.

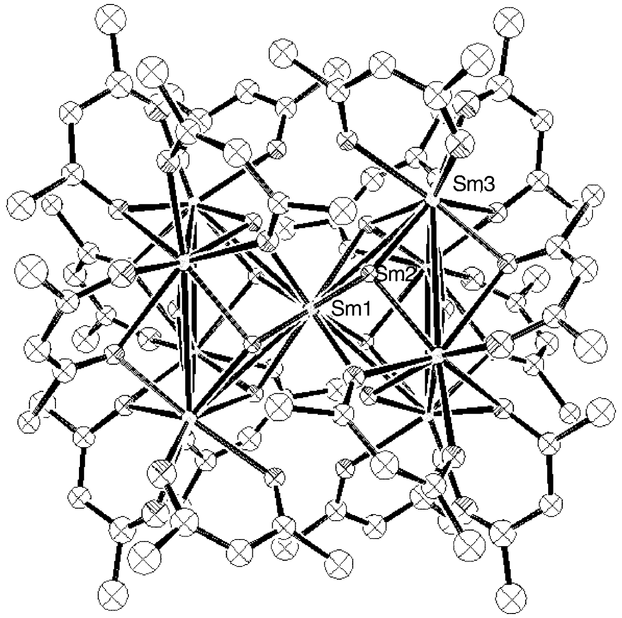

Fig. 1. An ORTEP drawing of Sm derivative (**1a**). Thermal ellipsoids are represented at 50% probability.

The barrels contain two alternative positions of the atoms in the clusters with a ratio of occupancy (70 and 30%), consequent to a rotation of about 45° of the atoms in the cluster, around an axis passing through the central Sm and the μ_4OH moiety (in Fig. 1, for sake of clarity, only the predominant structure is shown).

The molybdenum atoms lie on a crystallographic binary axis at a distance of 3.30(1) Å characteristic for a bent hydrogen bridge (the H position is not detectable) and the ten carbonyls are in staggered position as in the cromium and tungsten derivatives.

4.2. FTIR

FTIR absorption signals of species **1a–e** and **2a** in nujol mulls are listed in Table 4 and their values assigned to the particular bonds involved. All the new species show the characteristic hydroxide sharp band around 3570 cm^{-1} and a broad band in the range 3340–3350 cm^{-1}, respectively, assigned to the μ_4OH and μ_3OH stretching modes [27,28].

Table 4
FTIR data (cm^{-1}), nujol mulls, for (**1a**–**e**) and complex (**2a**)

	$\nu_{1,OH}$	$\nu_{2,OH}$	ν_{CO} metal carbonyl				$\nu_{C=C}$, $\nu_{C=O,acac}$	$\nu_{C=O}$, $\nu_{C=C,acac}$	ν_{C-CH_3} $\nu_{C=C,acac}$	$\nu_{CH_3,acac}$	$\nu_{C=C}$ $\nu_{C=O\ acac}$	acac ring vibration	$\nu_{\delta MCO}$
			$(A_1)_1$	E	B_2	$(A_1)_2$							
1a	3576w	3339b	2033w	1942s	1905w	1869s	1618s 1589s	1514s	1257m	1016m	922m	656w	594w
1b	3578w	3337b	2033w	1944s	1905w	1869s	1618s 1589s	1522s	1259m	1016m	922m	658w	594w
1c	3577w	3339b	2035w	1944s	1905w	1871s	1622s 1595s	1522s	1265m	1020m	922m	656w	592w
1d	3566w	3350b	2033w	1944s	1905w	1870s	1618s 1595s	1518s	1261m	1020m	924m	658w	592w
1e	3587w	3339b	2035w	1944s	1905w	1871s	1622s 1595s	1522s	1265m	1018m	926m	661w	594w
2a	3576w	3346b	2033w	1940s	–	1869s	1618s 1591s	1522s	1258m	1016m	922m	663w	598w

s, strong; m, medium; w, weak; b, broad.

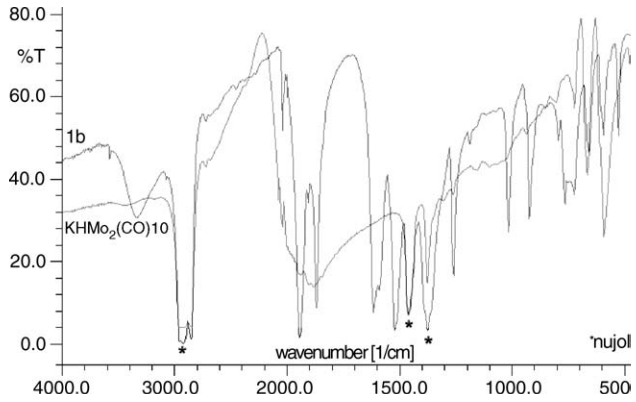

Fig. 2. Comparison IR spectra (nujol mull) of **1b** and $KHMo_2(CO)_{10}$.

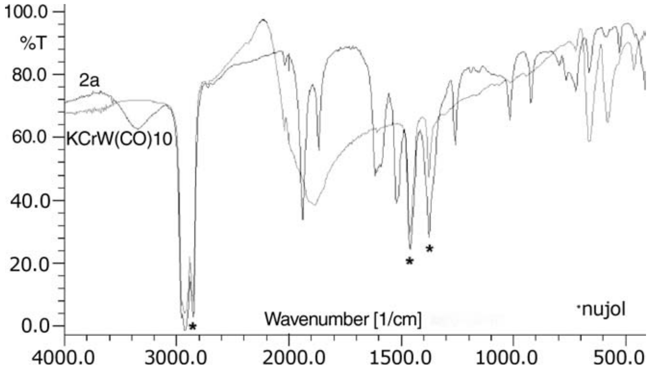

Fig. 3. Comparison IR spectra (nujol mull) of **2a** and $KHCrW(CO)_{10}$.

Although species **2a** like its chromium and tungsten homonuclear analogous clusters [29,30] shows only three peaks in the ν(CO) region due to the $(A_1)_1$ E and $(A_1)_2$ stretching modes of square piramidal (C_{4v}) arrangement of MCO_5 fragments, species **1a**–**e** show an additional signal at 1905 cm^{-1} assignable to B_2 mode. The B_2 mode is normally active in the Raman spectrum only, but small distortion in the structure can impart infrared activity [31], whereas bending mode of MCO bonds is around 590 cm^{-1}. A comparison of the spectra (nujol mull) of species **1b** and **2a** with respective counter ions as potassium salts, $KMo_2(CO)_{10}(\mu\text{-H})$ and $KCrW(CO)_{10}(\mu\text{-H})$, is reported in Figs. 2 and 3. The β-dichetonate ligand displays vibrational peaks in the fingerprint region between 1600 and 500 cm^{-1}.

5. Conclusions

The crystallographic results that give the most interesting information about this novel series of isostructural families in the cluster lanthanide series, have shown as the change of the metal: W, Cr or Mo in the $[M_2(CO)_{10}(\mu\text{-H})]^-$ counter anions do not influence the formation of these novel Ln clusters. The only significant difference is in a more symmetric arrangement of the atoms in the clusters for the tungsten, and molybdenum series.

Acknowledgment

The authors are grateful to the MIUR for financial support.

References

[1] X.M. Chen, M.S.J. Aubin, Y.L. Wu, Y.S. Yang, T.C.W. Mak, D.N. Hendrickson, J. Am. Chem. Soc. 117 (1995) 9600.
[2] X.M. Chen, Y.Y. Yang, Chin. J. Chem. 18 (2000) 664.
[3] P. Cheng, D.Z. LiaoRao, Chin. J. Chem. 19 (2001) 208.
[4] Q.Y. Chen, Q.H. Luo, Z.L. Wang, J.T. Chen, J. Chem. Soc., Chem. Commun. (2000) 1033.
[5] T. Shiga, M. Ohba, H. Okawa, Inorg. Chem. 43 (2004) 4435.
[6] C. Benelli, D. Gatteschi, Chem. Rev. 102 (2002) 2369.
[7] M. Sakamoto, K. Manseki, H. Okawa, Coord. Chem. Rev. 219–221 (2001) 379.
[8] L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge, G.K.L. Wong, Chem. Mater. 12 (2000) 2268.
[9] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, second ed., Kluwer Academic, Plenum Publishers, New York, 1999.
[10] P. Caravan, J.J. Ellison, T.J. Mc Murry, R.B. Lauffer, Chem. Rev. 99 (1999) 2293.
[11] B. Du, E.A. Meyers, S.G. Shore, Inorg. Chem. 39 (2000) 4639.
[12] D. Deng, et al., J. Chem. Soc. Dalton Trans. 33 (1994) 1665.
[13] H. Deng, S.G. Shore, J. Am. Chem. Soc. 113 (1991) 8538.
[14] B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, G.X. Xu, Angew. Chem., Int. Ed. 39 (2000) 3644.
[15] (a) S.A. Schuetz, V.W. Day, J.L. Clark, J.A. Belot, Inorg. Chem. Commun. 5 (2002) 706;
(b) R.Y. Wang, H.D. Selby, H. Liu, M.D. Carducci, T.Z. Jin, Z.P. Zheng, J.W. Anthis, R. Staples, J. Inorg. Chem. 41 (2002) 278;
(c) B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, New J. Chem. 24 (2000) 251;
(d) R.Y. Wang, Z.P. Zheng, T.Z. Jin, R. Staples, J. Angew. Chem., Int. Ed. 38 (1999) 1813;
(e) Z.P. Zheng, Chem. Commun. (2001) 2521;
(f) A.W.H. Lam, W.T. Wong, G.H. Wen, X.X. Zhang, S. Gao, New J. Chem. 25 (2001) 531.
[16] R.G. Xiong, J.L. Zuo, Z. Yu, X.Z. You, W. Chen, Inorg. Chem. Commun. 2 (1999) 490.
[17] D.S. Zhang, B.Q. Ma, T.Z. Jin, S. Gao, C.H. Yan, T.C.W. Mak, New J. Chem. 24 (2000) 61.
[18] D. Freedman, S. Sayan, T.J. Emge, M. Croft, J.G. Brennan, J. Am. Chem. Soc. 121 (1999) 11713.
[19] G. Xu, Z.M. Wang, Z. He, Z. Lu, C.S. Liao, C.H. Yan, Inorg. Chem. 41 (2002) 6802.
[20] M.R. Bürgstein, P.W. Roesky, Angew. Chem., Int. Ed. 39 (2000) 549.
[21] X.J. Zheng, L.P. Jin, S. Gao, Inorg. Chem. 43 (2004) 1600.
[22] M.D. Grillone, M. Addamo, M. Volpe, J. Alloys Compd. 61 (2001) 323.
[23] M. Addamo, G. Bombieri, E. Foresti, M.D. Grillone, M. Volpe, Inorg. Chem. 43 (2004) 1603.
[24] M. Volpe, G. Bombieri, D.A. Clemente, E. Foresti, M.D. Grillone, J. Alloys Compd. 374 (2004) 382.
[25] M.D. Grillone, G. Terranova, F. Genel Ricciardiello, Synth. Methodol. Inorg. Chem. 7 (1997) 240.
[26] G.M. Sheldrick, C. Kruger, R. Goddard, in: Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and

Database, Clarendon Press, Oxford, Oxford University Press, New York, 1985.

[27] M.D. Grillone, L. Palmisano, Transition Met. Chem. 14 (1989) 81.

[28] S.J. Lyle, M.M. Rahman, Talenta 10 (1963) 1177.

[29] T. Dubè, S. Gambarotta, G. Yap, Organometallics 17 (1998) 3967.

[30] K. Nakamoto, in :Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., Wiley, New York, 1986.

[31] P.S. Braterman, in: Metal Carbonyl Spectra, Academic Press, London, New York, 1975.