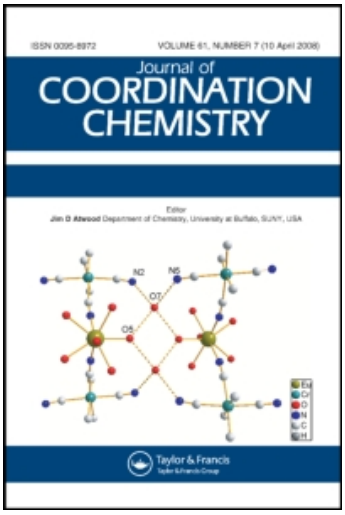

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A Novel Supramolecular Structure for a Lanthanum Picrate

Yanling Zhang[a]; Weisheng Liu[a]; Yawen Wang[a]; Ning Tang[a]; Minyu Tan[a]; Kaibei Yu[b]
[a] Department of Chemistry, Lanzhou University, Lanzhou, P.R. China [b] Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu, P.R. China

Online publication date: 15 September 2010

To cite this Article Zhang, Yanling , Liu, Weisheng , Wang, Yawen , Tang, Ning , Tan, Minyu and Yu, Kaibei(2002) 'A Novel Supramolecular Structure for a Lanthanum Picrate', Journal of Coordination Chemistry, 55: 11, 1293 — 1299
To link to this Article: DOI: 10.1080/0095897021000036415
URL: http://dx.doi.org/10.1080/0095897021000036415

J. Coord. Chem., 2002, Vol. 55(11), pp. 1293–1299

Taylor & Francis
Taylor & Francis Group

A NOVEL SUPRAMOLECULAR STRUCTURE FOR A LANTHANUM PICRATE

YANLING ZHANG[a], WEISHENG LIU[a,*], YAWEN WANG[a], NING TANG[a], MINYU TAN[a] and KAIBEI YU[b]

[a]*Department of Chemistry, Lanzhou University, Lanzhou 730000, P.R. China;* [b]*Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu 610041, P.R. China*

(Received 18 October 2001; In final form 23 April 2002)

A new complex of lanthanum picrate with *N*,*N*′-diethyl-*N*,*N*′-diphennyl-3-oxapentanediamide (L) was synthesized and its structure determined by X-ray diffraction measurements. It crystallizes as the ten-coordinate complex $La(pic)_3L_2$ in the triclinic space group $P\bar{1}$ with $a = 12.140(2)$, $b = 14.250(2)$, $c = 20.333(2)$ Å, $\alpha = 101.400(10)$, $\beta = 99.390(10)$, $\gamma = 102.400(10)^\circ$, $U = 3289.1(8)$ Å^3, $Z = 2$, $D_c = 1.519$ g cm^{-3}. The complex possesses a novel ladder-like 2-D supramolecular structure directed by π–π interactions.

Keywords: Lanthanum picrate; Noncyclic polyether; Complex; π–π interactions; Crystal structure

INTRODUCTION

Molecular self-assembly has emerged in recent years as an attractive approach to the fabrication of new materials [1,2]. This involves the spontaneous aggregation of molecular building blocks that recognize each other through multiple molecular recognition sites to form extended architectures, and weaker intermolecular interactions, such as hydrogen bonds and π–π stacking, play an important role [3–5]. In biology, π–π interaction of aromatic molecules occurs on several levels. Key examples are vertical base–base interaction in DNA, intercalation of drugs into DNA, tertiary structures of proteins, and porphyrin aggregation. Recently, a topic of considerable interest in the field of luminescent metallo-supramolecular complexes is the use of intermolecular energy transfer through π–π stacking between planar aromatic ligands [6–8]. In the present work, we demonstrate how the π–π stack is the effective interaction in self-assembly aggregations.

We have chosen an aromatic anion, picrate (pic.), and a noncyclic polyether, *N*,*N*′-diethyl-*N*,*N*′-diphennyl-3-oxapentanediamide (L), as ligand. It has been reported that this kind of noncyclic polyether containing an amide shows high complexation selectivity, making them suitable reagents for the extraction and analysis (ion-selective electrodes) of lanthanide ions [9,10]. By selective coordination and π–π recognition

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0095897021000036415

stacking in acetonitrile solution, a ladder-like 2-D supramolecular complex $[La(pic)_3L_2]$ is formed in this case.

EXPERIMENTAL

Materials and Methods

Lanthanide picrate [11] and L [12] were prepared according to literature methods. All commercially available chemicals were of reagent grade and were used without further purification. The metal ion was determined by EDTA titration using xylenol orange as indicator. C, N and H were determined using a Vario EL instrument.

$[La(pic_3)L_2]$

A solution of 0.2 mmol L in 10 cm^3 of ethanol was added dropwise to a solution of 0.1 mmol lanthanide picrate in 5 cm^3 of ethanol. The mixture was stirred at room temperature for 4 h. The precipitated solid complex was filtered, washed with ethanol and dried in *vacuo* over P_4O_{10} for 48 h. All the complexes were obtained as yellow powders. A yellow crystal of $[La(pic_3)L_2]$ suitable for single-crystal X-ray diffraction was obtained by slowly evaporating the MeCN solution of the appropriate product.

Structure of $[La(pic_3)L_2]$

For the lanthanum complex, intensity data were measured at 296(2) K on a P4 four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation, using a ω–2θ scan. Lorentz and polarization corrections were applied, but no absorption correction was made. A summary of crystallographic data and details of the structure refinement is given in Table I.

The structure was solved by the Patterson method and subsequent difference Fourier techniques, and refined by block-matrix least-squares procedures. Nonhydrogen atoms were refined anisotropically, final $R = 0.0281$, $wR = 0.0664$. The highest peak in the final difference Fourier was 0.413 e$Å^{-3}$. All calculations were performed on an Eclipse/S 140 computer with the SHELXS-97 package. In the final refinement the weighing scheme $w = [\sigma^2(F) + 0.00010F^2]^{-1}$ $\{1 - \exp[-5(\sin\ \theta/\lambda)^2]\}$ was used. Final atomic coordinates are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structure factors are available as supplementary data from W.L. upon request.

RESULTS AND DISCUSSION

The complex $[La(pic)_3L_2]$ is soluble in DMF, DMSO, MeCN and $CHCl_3$, but sparingly soluble in benzene, Et_2O and cyclohexane. Conductivity measurements for the complex in MeCN solution gave a value of 77.4 [Λm/S cm^2 mol^{-1}], indicating that the complex is a nonelectrolyte [13].

TABLE I Crystal data and structure refinement details for the complex $La(pic)_3L_2$

Empirical formula	C58 H54 La N13 O27
Temperature (K)	296(2) K
Crystal color	Yellow
Crystal size (mm)	$0.50 \times 0.52 \times 0.44$ mm
Formula weight	1504.05
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	12.140(2)
b (Å)	14.250(2)
c (Å)	20.333(2)
α (°)	101.400(10)
β (°)	99.390(10)
γ (°)	102.400(10)
V (Å^3)	3289.1(8)
Z	2
Density(calculated)(g/cm^3)	1.519
F(000)	1532
Radiation, λ(Å)	0.71073
Reflections collections	12508
Independent reflection	11515
θ range for data collection	1.51–25.00
Index range	$0 \le h \le 14$ $-16 \le k \le 16$ $-24 \le l \le 23$
Goodness-of-fit on F^2	1.041
$R[I > 2\sigma(I)]$	$R = 0.0281$ $wR = 0.0664$
R(all data)	$R = 0.0357$ $wR = 0.0683$
Largest difference peak and hole [e Å^{-3}]	0.413, −0.403

X-Ray Structure

Figure 1 shows the structure of $[La(pic)_3L_2]$, which is ten-coordinated by six oxygen atoms from L, and four from one bidentate (O7, O13), and two unidentate (O14, O21) pic ligands. The coordination geometry is best described as a distorted bicapped dodecahedron with C_1 symmetry. Two L molecules wrap around the La(III) ion and form a ring-like coordination structure. One unidentate (C53–C58) pic is situated above the plane and the other unidentate (C47–C52) and the bidentate (C41–C46) pic groups lie underneath. The average distance between the lanthanum atom and the coordinated oxygen atoms is 2.602 Å, while the different types of four average bond lengths are in the order La–O(C–O, pic) < La–O(C=O, L) < La–O(C–O–C) < La–O(NO_2, pic) (see Table III).

There are three types of π–π stacking of picrates in this structure. In one complex molecule (Laa) the bidentate (C41a–C46a) and a unidentate (C47a–C52a) pics form a *gauche* stack (denoted by UBG, shown in Fig. 2) along the y-axis; the intercentroid distance and the dihedral angle between the two pics are 3.40 Å and 6.1°. Above the unidentate pic (C47a–C52a), another unidentate ligand from an adjacent complex molecule (Lae) parallels it at a distance of 3.46 Å and with a dihedral angle of 0.0°, forming a *trans* stack (UUT, Fig. 2). Below the bidentate pic (C41A–C46A), another bidentate ligand from an adjacent molecule (Laf) parallels it (distance 3.41 Å; dihedra angle: 0.0°), forming a *trans* stack (BBT, Fig. 2). The other unidentate pic (C53a–C58a) in the molecule Laa is situated along a diagonal of x and z and parallels another unidentate pic from an adjacent molecule

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)(Å^2)	*Atom*	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)(Å^2)
La	c2666(1)	1336(1)	2740(1)	36(1)	C(11)	1959(2)	3398(2)	2141(1)	43(1)
O(1)	4355(1)	1911(1)	2225(1)	49(1)	C(12)	1258(2)	3154(2)	2654(1)	42(1)
O(2)	2895(1)	2956(1)	2242(1)	43(1)	C(13)	186(2)	4307(2)	2348(2)	59(1)
O(3)	1464(2)	2551(1)	2984(1)	50(1)	C(14)	628(3)	5308(2)	2641(2)	92(1)
O(4)	754(2)	574(1)	3011(1)	55(1)	C(15)	381(5)	5963(3)	2254(4)	141(2)
O(5)	1574(1)	−730(1)	2390(1)	48(1)	C(16)	−250(5)	5643(5)	1607(4)	152(3)
O(6)	3258(2)	−5(1)	1900(1)	56(1)	C(17)	−691(5)	4655(5)	1331(3)	131(2)
O(7)	4171(2)	2679(1)	3584(1)	54(1)	C(18)	−480(3)	3978(3)	1702(2)	84(1)
O(8)	6092(5)	3964(6)	3400(3)	106(2)	C(19)	−325(3)	3370(3)	3224(2)	82(1)
O(9)	7475(4)	3851(12)	4165(4)	185(5)	C(20)	78(4)	4035(4)	3907(2)	150(2)
O(10)	7057(3)	5148(2)	6446(1)	128(1)	C(21)	−1142(2)	−1435(2)	3384(2)	60(1)
O(11)	5455(3)	4607(2)	6722(1)	118(1)	C(22)	−566(3)	−1905(2)	3799(2)	71(1)
O(12)	2080(2)	3142(2)	4847(1)	94(1)	C(23)	−1078(4)	−2860(3)	3828(2)	94(1)
O(13)	2366(2)	1939(1)	4124(1)	62(1)	C(24)	−2160(5)	−3309(3)	3462(3)	113(2)
O(14)	3603(2)	446(1)	3507(1)	56(1)	C(25)	−2754(4)	−2847(3)	3064(2)	117(2)
O(15)	5571(3)	43(4)	3074(2)	170(2)	C(26)	−2253(3)	−1889(3)	3015(2)	87(1)
O(16)	6695(3)	1480(4)	3354(2)	162(2)	C(27)	−1110(3)	378(2)	3603(2)	71(1)
O(17)	7888(3)	2510(2)	5875(2)	136(1)	C(28)	−519(3)	909(3)	4320(2)	94(1)
O(18)	6574(3)	2303(2)	6464(2)	135(1)	C(29)	298(2)	−268(2)	3055(1)	48(1)
O(19)	2644(2)	908(2)	5322(1)	113(1)	C(30)	769(2)	−1111(2)	2762(1)	53(1)
O(20)	2281(2)	−209(2)	4379(1)	86(1)	C(31)	2181(2)	−1426(2)	2156(1)	53(1)
O(21)	1371(2)	1065(1)	1603(1)	53(1)	C(32)	3081(2)	−907(2)	1837(1)	47(1)
O(22)	−779(2)	1310(2)	1698(2)	111(1)	C(33)	3352(3)	−2523(2)	1385(2)	64(1)
O(23)	−1675(2)	−57(3)	1903(1)	124(1)	C(34)	2564(3)	−3107(2)	811(2)	82(1)
O(24)	−2101(4)	−2924(2)	52(2)	170(2)	C(35)	2286(4)	−4117(3)	715(2)	98(1)
O(25)	−639(4)	−3047(2)	−422(2)	158(2)	C(36)	2817(4)	−4545(3)	1180(2)	101(1)
O(26)	2680(3)	−357(3)	118(2)	148(1)	C(37)	3591(4)	−3976(3)	1745(2)	105(1)
O(27)	2640(2)	1087(2)	635(1)	103(1)	C(38)	3871(4)	−2941(2)	1852(2)	87(1)
N(1)	5554(2)	2844(2)	1738(1)	55(1)	C(39)	4554(5)	−1010(3)	1169(3)	160(3)
N(2)	409(2)	3605(2)	2734(1)	53(1)	C(40)	5481(4)	−1242(4)	1166(4)	197(3)
N(3)	−607(2)	−454(2)	3342(1)	57(1)	C(41)	4575(2)	3169(2)	4194(1)	46(1)
N(4)	3649(2)	−1459(2)	1487(1)	68(1)	C(42)	5745(2)	3750(2)	4437(1)	56(1)
N(5)	6492(2)	3866(3)	3946(2)	87(1)	C(43)	6225(3)	4219(2)	5114(2)	64(1)
N(6)	6050(3)	4675(2)	6305(2)	86(1)	C(44)	5545(3)	4189(2)	5589(1)	60(1)
N(7)	2706(2)	2733(2)	4549(1)	56(1)	C(45)	4391(3)	3717(2)	5398(1)	56(1)
N(8)	5946(3)	831(4)	3452(2)	105(1)	C(46)	3937(2)	3226(2)	4725(1)	48(1)
N(9)	6900(3)	2204(2)	5924(2)	94(1)	C(47)	4349(2)	727(2)	4063(1)	50(1)
N(10)	2920(2)	488(2)	4812(1)	68(1)	C(48)	5564(3)	1036(2)	4093(2)	62(1)
N(11)	−991(2)	418(3)	1639(1)	80(1)	C(49)	6373(3)	1513(2)	4680(2)	71(1)
N(12)	−1126(5)	−2593(2)	−29(2)	122(2)	C(50)	6040(3)	1664(2)	5293(2)	64(1)
N(13)	2245(3)	201(3)	454(1)	81(1)	C(51)	4920(3)	1319(2)	5329(1)	61(1)
C(1)	5801(2)	3642(2)	1406(2)	58(1)	C(52)	4098(2)	845(2)	4735(1)	52(1)
C(2)	6467(3)	4554(3)	1780(2)	86(1)	C(53)	758(2)	298(2)	1173(1)	48(1)
C(3)	6747(4)	5307(3)	1450(3)	113(2)	C(54)	−399(2)	−152(2)	1191(1)	56(1)
C(4)	6387(4)	5129(4)	764(3)	116(2)	C(55)	−1006(3)	−1078(2)	820(2)	72(1)
C(5)	5726(4)	4224(4)	384(2)	107(1)	C(56)	−504(4)	−1593(2)	362(2)	79(1)
C(6)	5417(3)	3474(3)	712(2)	78(1)	C(57)	546(3)	−1171(2)	247(1)	74(1)
C(7)	6415(3)	2261(3)	1816(2)	75(1)	C(58)	1153(3)	−246(2)	626(1)	60(1)
C(8)	6421(4)	1595(3)	1150(2)	113(1)	O(8′)	6290(20)	3390(40)	3362(11)	182(16)
C(9)	4583(2)	2611(2)	1957(1)	44(1)	O(9′)	7385(18)	4490(19)	4048(12)	146(11)
C(10)	3735(2)	3233(2)	1869(1)	50(1)					

(Lad) (distance: 3.56 Å; dihedra angle: 0.0°), also forming a *trans* stack (BBT). All picrates in the structure are selectively arranged in fixed order by π–π stacking. Within each complex molecule, the stack is in the *gauche* pattern between unidentate and bidentate pics (UBG), while the intermolecular pic ligands stack

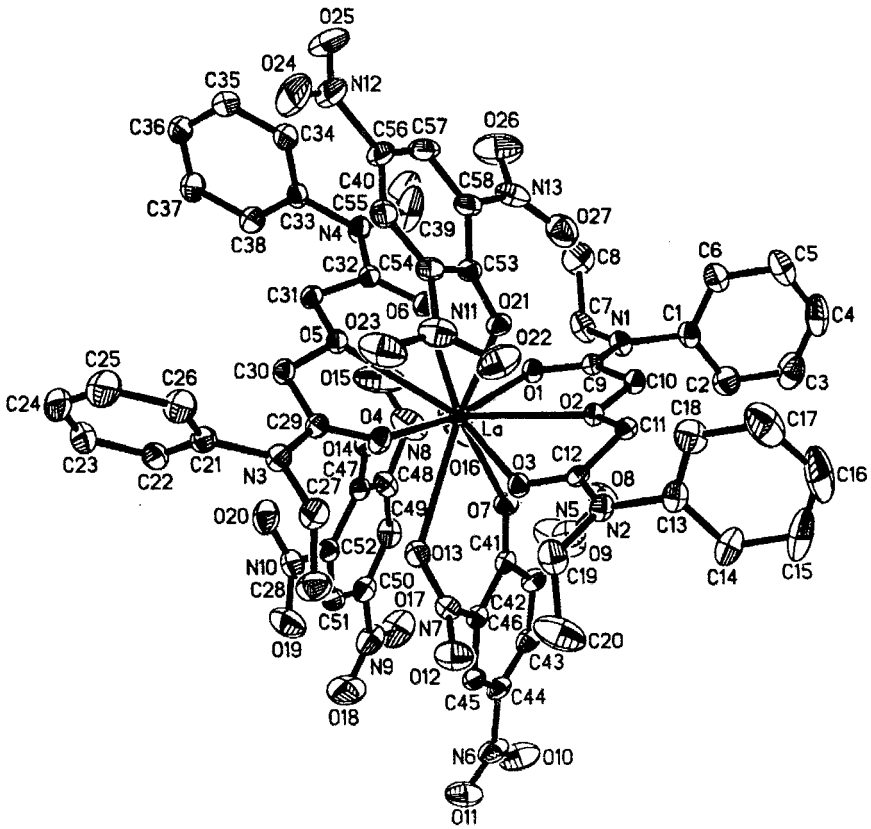

FIGURE 1 The structure of $[La(pic_3)L_2]$.

TABLE III Selected bond lengths (Å) and angles (°) for $La(pic)_3L_2$

Bond lengths			
La–O(1)	2.506(17)	La–O(6)	2.6051(17)
La–O(2)	2.6788(15)	La–O(7)	2.4742(17)
La–O(3)	2.5219(19)	La–O(13)	2.882(2)
La–O(4)	2.5383(17)	La–O(14)	2.4807(16)
La–O(5)	2.8493(16)	La–O(21)	2.4829(16)
Bond angles			
O(7)–La–O(14)	76.68(6)	O(1)–La–O(2)	58.76(5)
O(7)–La–O(1)	69.13(6)	O(3)–La–O(2)	58.11(5)
O(21)–La–O(3)	77.52(6)	O(4)–La–O(5)	55.25(5)
O(21)–La–O(4)	80.41(6)	O(6)–La–O(5)	55.07(5)
O(14)–La–O(6)	76.29(6)	O(7)–La–O(13)	60.35(5)

trans between two unidentate (UUT) or bidentate (BBT) groups. The whole stack sketch in the unit cell is shown in Fig. 2. The resultant 2-D supramolecular structure includes ladder-like arrays along the *y*-axis, and a chain along the diagonal between *x* and *z* (see Fig. 3).

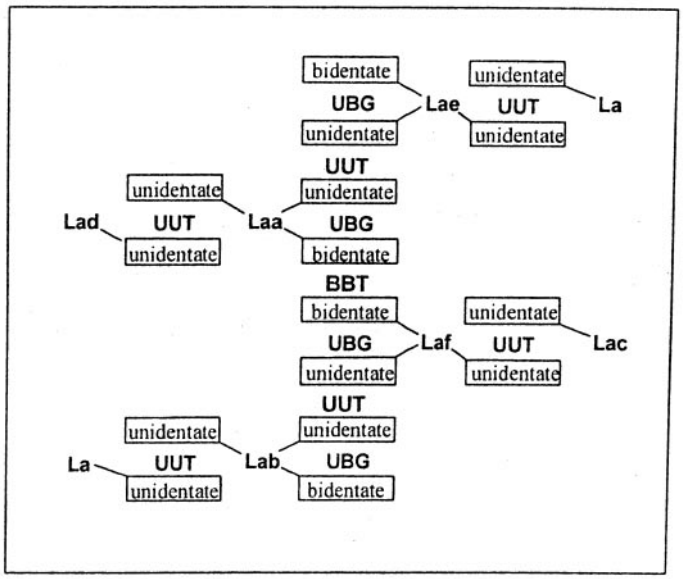

FIGURE 2 A π–π stack sketch for $[La(pic)_3L_2]$ in the unit cell.

FIGURE 3 View of the 2-D ladder-like supramolecular structure of $[La(pic)_3L_2]$ along the *y*-axis.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (project 20071015) and the Foundation for University Key Teachers by the Ministry of Education of China.

References

[1] J.M. Lehn (1995). *Supramolecular Chemistry*, Chapter 9. VCH, Weinheim.
[2] (a) K. Nakasuji, K. Sugiur, T. Kitugawa, J. Toyoda, A. Kawamoto and J. Tanka (1991). *J. Am. Chem. Soc*., **113**, 1862; (b) A. Aouxel (1992). *Acc. Chem. Res*., **25**, 328.
[3] H.Y. Shen, D.Z. Lao, Z.H. Jiang, S.P. Yan, B.W. Sun, G.L. Wang, X.K. Yao and H.G. Wang (1998). *Chem. Lett*., 469.
[4] L. Stelzig, A. Steiner, B. Chansou and J.P. Tuchagues (1998). *Chem. Commun*., 771.
[5] I. Dance and M. Scudder (1996). *Chem. Eur. J*., **2**, 481.
[6] V. Balzani, J.M. Lehn, J.V. Loosdrecht, A. Mecati, N. Sabbatini and R. Ziessel (1991). *Angew. Chem., Int. Ed. Engl*., **30**, 190.
[7] N.W. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenou, E.A. Plummer, K. Rissanen and P. Saarenketo (2000). *J. Chem. Soc., Dalton Trans*., 1447.
[8] R. Wietzke, M. Mazzanti, J.M. Latour and J. Pécaut (1999). *Chem. Commun*., 209.
[9] Y.S. Yang and Y.Z. Ding (1984). *J. Nucl. Radiochem*., **6**, 196.
[10] S.X. Liu, W.S. Liu and M.Y. Tan (1996). *J. Coord. Chem*., **39**, 105.
[11] Y.C. Tian, Y.Q. Liang and J.Z. Ni (1988). *Chem. J. Chin. Univ*., **9**, 113.
[12] G.Z. Tan, J.Z. Xu, Z.Q. Yao and F.S. Zhang (1983). *Huaxue Shiji*, **5**, 100.
[13] W.J. Greary (1971). *Coord. Chem. Rev*., **79**, 81.