Sains Malaysiana 38(2)(2009): 185–190

Synthesis and Structural Studies of Lanthanum(Iii) Dialkyldithiocarbamates 1,10-Phenantroline

(Sintesis dan Kajian Struktur Lantanum(Iii) Dialkilditiokarbamat 1,10 Fenantrolin)

IBRAHIM BABA, INDAH RAYA & BOHARI MOHD YAMIN

ABSTRACT

A new series of lanthanum dialkyldithiocarbamate complexes with 1,10-phenantroline were successfully synthesized using in situ methods. These complexes were characterized using elemental analysis, infrared, thermogravimetric analysis and conductivity. Microelemental analysis data were in agreement with the general formula La(S_2CNR'R")$_3$phen (R'=ethyl, methyl; R"=butyl, heptyl, isopropyl, isobutyl, benzyl and cyclohexyl; phen = 1,10-phenantroline). Infrared spectra of complexes showed the thioureide ν(C-N) bands were in the region of 1450 - 1482 cm^{-1}. The single ν(C-S) bands appeared in the region of 959 – 997 cm^{-1} and ν(C-H) bands in the region of 2918-2955 cm^{-1}. The crystal structure of tris(N,N-ethylbenzyldithiocarbamate)(1,10-phenantroline)lantanum(III) adopts an orthorombic system (space group Pccn) with a distorted dodecahedron geometry with a = 19.865(5) Å , b = 42.803(10) Å, c = 10.657(3) Å, α = β = γ= 90^o and Z = 9. Three dithiocarbamates and one phenanthroline ligands were coordinated to the central La atom in bidentate manner.

Keywords: Lanthanum; dithiocarbamate; crystal structure

ABSTRAK

Satu siri baru kompleks lantanum dialkilditiokarbamat dan 1,10-fenantrolin telah berjaya disintesis secara in-situ. Kompleks telah diciri dengan analisis unsur, spektroskopi inframerah, analisis termogravimetri dan pengukuran konduktiviti. Hasil analisis unsur menunjukkan formula umum adalah La(S_2CNR'R")$_3$phen (R' = metil, etil; R" = butil, heptil, isopropil, isobutil, benzil dan sikloheksil; phen = fenantrolina). Spektrum inframerah kompleks menunjukkan jalur tioureida ν(C-N) berada di sekitar 1450-1482 cm^{-1}. Manakala jalur tunggal ν(C-S) pula berada di kawasan 959-997 cm^{-1} dan jalur ν(C-H) berada di kawasan 2918-2957 cm^{-1}. Struktur hablur tris(N,N-etilbenzilditiokarbamat)(1,10-fenantrolin) lantanum(III) dengan sistem hablur ortorombik (kumpulan ruang Pccn) dengan geometri dodekahedron terherot dengan a = 19.865(5) Å, b = 42.803(10) Å, c = 10.657(3) Å, α = β = γ = 90^o dan Z = 9. Tiga molekul ditiokarbamat dan satu molekul fenantrolina membentuk ikatan kelat kepada atom La secara bidentat.

Kata kunci: Lantanum; ditiokarbamat; struktur hablur

INTRODUCTION

Dithiocarbamates are among the most important nitrogen/sulfur donor ligands. Dithiocarbamate complexes are of great interest due to their chemical and biological properties and widely used in industries of agriculture, pharmaceutical and medicine (Coucovanis & Fackler 1976; Hursthouse et al. 1992). Almost all of the dithiocarbamate complexes with lanthanide are prepared in inert atmosphere using anhydrous lanthanides salts (Siddal & Steward 1970; Tang et al. 1991; Zhu et al. 1993). Su et al. (1997) has reported the synthesis of lanthanide dithiocarbamate 1,10-phenantroline complexes with dialkyldithiocarbamate ligands (dialkyl = monomethyl, dimethyl and diethyl). However, another method to synthesize Ln(S_2CNR'R")$_3$phen (Ln = lanthanide) is by reacting of Ln(S_2CNR'R")$_3$ with 1,10-phenantroline (Tang et al. 1991). The latest report on lanthanide dithiocarbamate was by the reaction between potassium dithiocarbamate and gadolinium(III) chloride 1,10-phenantroline solutions to prepare Ga(S_2CNR'R")$_3$phen (Indah Raya et al. 2007).

This paper reports the synthesis and characterization of seven dialkyldithiocarbamate complexes of lanthanum(III) with various dithiocarbamate ligandsthe including x-ray structure of tris(*N,N*-ethylbenzyldithiocarbamate)(1,10-phenantroline)lantanum(III), La[S_2CN(C_2H_5)(C_7H_7)]$_3$phen.

MATERIALS AND METHODS

MATERIALS

All chemicals are purchased from suppliers as follows: acetonitrile (Hmbg Chemical), dialkylamine and ethanol (Fluka Chemical), carbon disulphide and methanol (Ajax Chemical Ltd), dichloromethane (R & M Chemical), lantanum(III) chloride and 1,10-phenantroline (Merck) and used as supplied without further purification.

INSTRUMENTATION

Elemental analysis was recorded on Fison EA1108, infrared spectra were recorded as KBr discs in the range 4000 – 500 cm^{-1} and with polyethylene (in Nujol mull) in the range of 500 - 200 cm^{-1} using Perkin Elmer FTIR Model GX. The melting point was determined using Electrothermal IA 9100. Thermal analysis was carried out on Mettler Toledo Model STGA/SDTA851. The electrical conductivity was measured by Philips conductivity bridge Model PR 9645. The X-ray structure determination was carried out by Bruker SMART APEX and the accompanying SHELXTL programming suite.

Room-temperature diffraction data for X-ray crystallography studies were collected on a Bruker SMART APEX area-detector diffractometer (Mo Kα radiation, λ=0.71073 Å) on a crystal with 0.45 x 0.19 x 0.04 mm dimensions over the 1.76< θ <25.0 range (Siemens 1996). The structure was solved and refined by using the SHELXS-97 (Sheldrick 1997). The final R ($I>2/\sigma(I)$) was 0.1096. All non-hydrogen atoms were refined anisotropically. The perspective view of the molecule was obtained using SHELXTL (Sheldrick 1996).

SYNTHESIS

The lanthanum dithiocarbamate complexes from various dialkylamines were prepared the same method reported previously by Indah Raya et al. (2007). A potassium dithiocarbamate was prepared by the reaction of an ethanolic solution of potassium hydroxide (30 mL) with dialkylamine (30 mmol) and carbon disulphide (30 mmol) at temperature below 10°C (Thorn & Ludwig 1962). Lanthanum(III) chloride solution (10 mmol) was added to 1,10-phenantroline (10 mmol) in boiling water to produce a lanthanide(III) chloride 1,10-phenantroline solution.

The dithiocarbamate complexes were synthesized by the reaction between potassium dithiocarbamate and lanthanum(III) chloride 1,10-phenantroline solutions at 40°C and allowed to cool down for precipitation. Recrystallization was performed from a mixture of dichloromethane and methanol (2:1 v/v). An outline of the reaction scheme is given in Figure 1.

RESULTS AND DISCUSSION

The elemental analysis data of complexes were in agreement with the general formula $La[S_2CNR'R'']_3phen$ [R' = ethyl, methyl; R" = butyl, heptyl, isopropyl, isobutyl, benzyl and cyclohexyl; phen = 1,10-phenantroline] (Table 1). The electrical conductivity data (Table 2) showed that all lanthanum(III) dithiocarbamate complexes were non-electrolytes. The molar conductance data were in the range of 42-51 $m.ohm^{-1}$ (< 65 m.ohm , indicating that all complexes were non-electrolytes and will imply the ligands were coordinated to the metal ions as uninegatively charged bidentate species (Su et al. 1997).

The infrared (IR) data of the complexes were tabulated in Table 3. The IR spectra showed C-H band in the range 2918 – 2957 cm^{-1} (Bellamy 1975) and La(M*i*Budtc)$_3$phen and La(E*i*Prdtc)$_3$phen were the highest due the steric

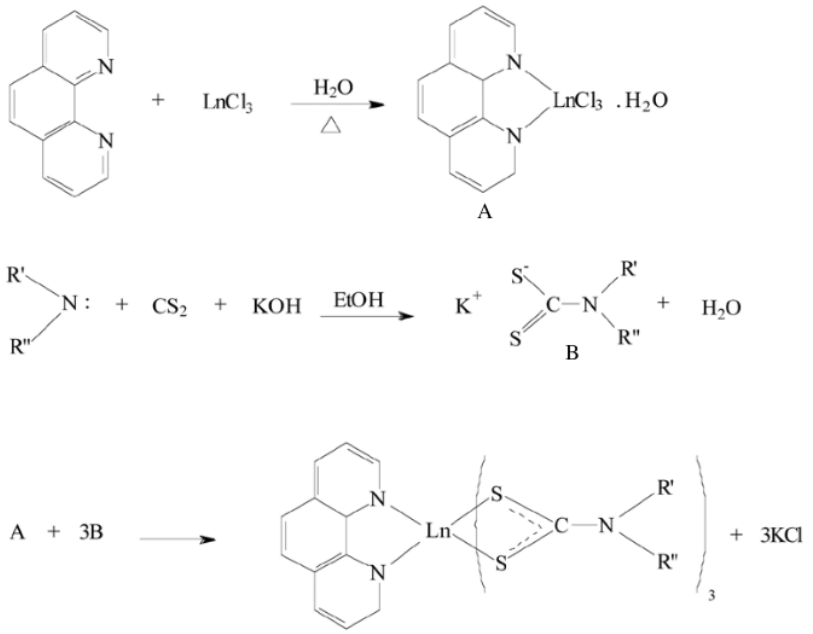

FIGURE 1. Reaction scheme for the synthesis of lanthanide complexes

TABLE 1. Analytical and physical data of $La(S_2CNR'R'')_3phen$

Complexes	Colour	Yield (%)	Melting point (°C)	Found (Calculated) (%)				
				C	H	N	S	La
La(EBudtc)3phen	White	66	91-93	41.92	5.75	9.59	22.44	15.56
				(46.62)	*(6.17)*	*(8.24)*	*(22.69)*	*(16.34)*
La(HpMdtc)3phen	White	42	116-118	50.98	7.35	7.43	21.45	15.08
				(50.25)	*(6.70)*	*(7.51)*	*(20.64)*	*(14.90)*
La(EiPrdtc)3phen	white	50	85-87	43.87	5.71	8.77	23.38	16.81
				(44.70)	*(5.50)*	*(8.69)*	*(23.87)*	*(17.23)*
La(MiBudtc)3phen	White	56	122-124	46.92	5.71	8.77	23.38	15.90
				(44.70)	*(5.50)*	*(8.69)*	*(23.87)*	*(17.23)*
La(MBzdtc)3phen	White	89	125-127	51.14	4.43	7.39	21.21	14.83
				(51.57)	*(4.22)*	*(7.71)*	*(21.19)*	*(15.30)*
La(EBzdtc)3phen	White yellow	72	113-115	52.75	4.82	7.82	18.47	15.43
				(51.47)	*(4.43)*	*(7.78)*	*(21.14)*	*(15.26)*
La(ECydtc)3phen	White	81	70-72	49.49	6.22	7.07	21.33	15.06
				(50.47)	*(6.30)*	*(7.55)*	*(20.73)*	*(14.96)*

E = ethyl; Bu = butyl; Hp = heptyl; M = methyl; Bz = benzyl; Pr = propyl; Cy = cyclohexyl; phen = 1,10-phenanthroline; dtc = dithiocarbamate

Table 2. Electrical conductivity of $La(S_2CNR'R'')_3phen$

Complexes	Electrical Conductivity Ω, (m.ohm -1)
La(EBudtc)3phen	42
La(HpMdtc)3phen	51
La(EiPrtc)3phen	42
La(MiBudtc)3phen	42
La(MBzdtc)3phen	49
La(EBzdtc)3phen	42
La(ECydtc)3phen	47

E = ethyl; Bu = butyl; Hp = heptyl; M = methyl; Bz = benzyl; Pr = propyl; Cy = cyclohexyl; dtc = dithiocarbamate

effect of the *iso* groups. The intense bands in the region of 1450 – 1470 cm^{-1} were for ν(C–N) modes of thioureide band, while ν(C=S) mode was appeared in the region 959 – 997 cm^{-1} (Brown 1976; Haas & Schwarz 1963). The presence of splitted ν(C=S) bands in the area of 959 – 997 cm^{-1} indicated a bidentate nature of the chelation of the dithiocarbamate ligands (Criado et al. 1990; Nomura et al. 1987).

The thermogram of La(M*i*Budtc)$_3$phen, La(EBzdtc)$_3$phen and La(MHpdtc)$_3$phen showed a decomposition temperature above 300°C which indicated the complexes possess good thermal stability, while the La(EBudtc)$_3$phen and La(ECydtc)$_3$phen showed similar trend which start to decompose at 160°C. However, La(MBzdtc)$_3$phen and La(E*i*Prdtc)$_3$phen complexes were less stable than others because they decomposed at below 110°C.

The data of important ^1H and ^{13}C NMR chemical shifts of the compounds were compiled in Table 4. The ^1H chemical shifts of the 1,10-phenantroline groups in the complexes were between 7.68 and 9.87 ppm. Overlapping of the signals occur when R" was also a phenyl and aryl groups. The data of ^{13}C chemical shifts of $N^{13}CS_2$ moiety appeared between 193 and 209 ppm. The high values of $N^{13}CS_2$ chemical shifts could be due to an increase of π-bond order in the whole NCS_2 moiety (Nomura et al. 1987). This suggested that the chelation of the nitrogen ligand to the lanthanum atom has promoted the delocalization of the unshared electron pair in the nitrogen atoms of the dithiocarbamate groups.

TABLE 3. Infrared data for La(S_2CNR'R'')$_3$phen

Complexes	Frequency (cm-1)				
	ν(C-H)	ν(C---N)	ν(C=S)	ν(La-N)	ν(La-S)
La(EBudtc)3phen	2930	1479	997	361	273
La(HpMdtc)3phen	2925	1482	981	364	272
La(EiPrdtc)3phen	2957	1482	988	362	273
La(MiBudtc)3phen	2955	1480	988	363	278
La(MBzdtc)3phen	2918	1478	990	364	272
La(EBzdtc)3phen	2927	1471	959	361	275
La(ECydtc)3phen	2930	1450	997	363	274

E = ethyl; Bu = butyl; Hp = heptyl; M = methyl; Bz = benzyl; Pr = propyl; Cy = cyclohexyl; phen = 1,10-phenanthroline; dtc = dithiocarbamate

TABLE 4. Selected ^{1}H and ^{13}C NMR data (δ, ppm) for La(S_2CNR'R'')$_3$phen

Formula	1H NMR (1,10-phenantroline)	13C NMR (N13CS2)
1,10-phenantroline	9.17, 7.61, 8.22, 7.76	-
La(EBudtc)3phen	9.21, 7.67, 8.27, 7.82	193.07
La(HMdtc)3phen	9.76, 7.68, 8.32, 7.81	207.59
La(EiPrdtc)3phen	9.19, 7.81, 8.58, 8.02	207.20
La(MiBudtc)3phen	9.87, 7.73, 8.40, 7.85	207.95
La(EBzdtc)3phen	9.80, 7.68, 8.33, 7.81	208.77
La(ECydtc)3phen	9.11, 7.78, 8.51, 8.00	206.23

E = ethyl; Bu = butyl; H = heptyl; M = methyl; Bz = benzyl; Pr = propyl; Cy = cyclohexyl; phen = 1,10-phenanthroline; dtc = dithiocarbamate

X-RAY CRYSTALLOGRAPHY

The La[$S_2CN(C_2H_5)(C_7H_7)$]$_3$phen complex crystallized in an orthorombic system with a space *Pccn* group. The crystal data and refinement parameter are given in Table 5. Selected bond distances and angles were compiled in Table 6. The molecular structure of the compound shown in Figure 2 supports the elemental and spectroscopic data given in Table 1, 2 and 3.

One phenantroline and three ethylbenzyldithiocarbamate ligands were chelated to lanthanum(III) centre in a bidentate manner via nitrogen and sulphur atoms respectively, in a distorted dodecahedron geometry. The bond angles of S(1)-La-S(2), S(3)-La-S(4), S(5)-La-S(6) were 62.47(8)°, 62.18(9)° and 61.65(8)°, respectively. The C-S bonds have an average distance of 1.34 Å and the mean of S–C–S angle was of 118.6°. The thioureide C–N bond distances

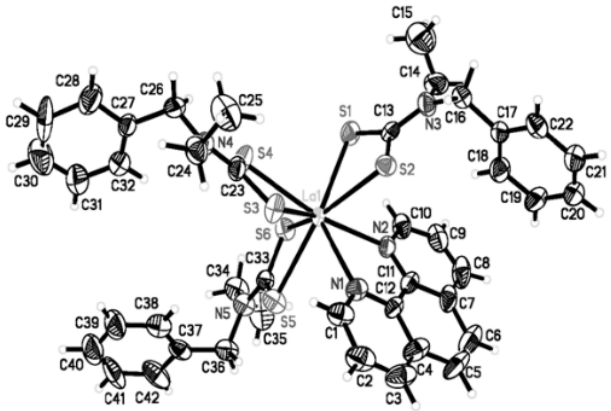

FIGURE 2. ORTEP Plot of lanthanum tris(*N,N*-ethylbenzyldithiocarbamate)1,10-phenantroline with displacement ellipsoids drawn at the 50% probability level

TABLE 5. Crystallographic data for $La[S_2CN(C_2H_5)(C_7H_7)]_3phen$

Compound	$La[S_2CN(C_2H_5)(C_7H_7)]_3phen$
Empirical Formula	$C_{42}H_{44}N_5S_6La$
Formula weight	844.33
Temperature	273 K
Wavelength A	0.71073
Crystal system	Orthorombic
Space group	Pccn
a Å	19.865(5)
b Å	42.803(10)
c Å	10.657(10)
α /°	90
β /°	90
γ /°	90
V (Å3)	9061(4)
Z	9
D/Mgm^{-3}	1.393
F (000)	3872
Crystal size	0.45 x 0.19 x 0.04 mm
Refinement method	Full matrix least-square
θ range (°)	1.76 - 25.00°
Final R indices I > 2σ(I)	$R_1 = 0.1096$, $wR_2 = 0.2230$

TABLE 6. Selected bond distances (Å) and angles (°) for $La[S_2CN(C_2H_5)(C_7H_7)]_3phen$

La(1)-N(1)	2.590(8)	N(2)-La(1)-N(1)	64.2(3)
La(1)-N(2)	2.572(8)	N(2)-La(1)-S(4)	155.2(2)
La(1)-S(1)	2.862(3)	N(1)-La(1)-S(4)	140.2(2)
La(1)-S(2)	2.827(3)	N(2)-La(1)-S(5)	92.0(2)
La(1)-S(2)	2.827(3)	N(1)-La(1)-S(5)	69.7(2)
La(1)-S(4)	2.807(3)	S(4)-La(1)-S(5)	94.71(12)
La(1)-S(5)	2.822(3)	N(2)-La(1)-S(2)	77.41(19)
La(1)-S(6)	2.894(3)	N(1)-La(1)-S(2)	80.5(2)
S(1)-C(13)	1.700(11)	S(4)-La(1)-S(2)	106.68(10)
S(2)-C(13)	1.713(11)	S(5)-La(1)-S(2)	150.05(9)
S(3)-C(23)	1.710(11)	N(2)-La(1)-S(3)	141.5(2)
S(4)-C(23)	1.696(11)	N(1)-La(1)-S(3)	81.4(2)
S(5)-C(33)	1.711(10)	S(4)-La(1)-S(3)	62.18(9)
S(6)-C(33)	1.705(10)	S(5)-La(1)-S(3)	91.84(10)
N(3)-C(13)	1.369(14)	S(2)-La(1)-S(3)	80.40(9)
N(4)-C(23)	1.337(12)	N(2)-La(1)-S(1)	78.9(2)
N(5)-C(33)	1.333(13)	N(1)-La(1)-S(1)	132.6(2)
		S(4)-La(1)-S(1)	81.56(11)
		S(5)-La(1)-S(1)	143.43(9)
		S(2)-La(1)-S(1)	62.47(8)
		S(3)-La(1)-S(1)	117.29(10)
		N(2)-La(1)-S(6)	82.58(19)
		N(1)-La(1)-S(6)	119.1(2)
		S(4)-La(1)-S(6)	79.70(9)
		S(5)-La(1)-S(6)	61.65(8)
		S(2)-La(1)-S(6)	141.75(8)
		S(3)-La(1)-S(6)	131.87(8)
		S(1)-La(1)-S(6)	81.98(9)

of N(3)-C(13), N(4)-C(23) and N(5)-C(33) were 1.369(14), 1.337(12) and 1.333(13) Å, respectively. These bonds were shorter than single bond C-N and suggested the existence of partial double bond character for (C…N) as indicated in infrared spectra data (1450 – 1482 cm^{-1}).

CONCLUSION

The lanthanum *tris*(N,N-*R*'*R*"dithiocarbamate)1,10-phenantroline series have been successfully synthesized and showed that the dithiocarbamate anions and 1,10-phenantroline were chelated to lanthanum center to form eight coordinated mixed-ligand compounds. The crystallographic studies of $La[S_2CN(C_2H_5)(C_7H_7)]_3$phen compounds showed the dithiocarbamate and nitrogen ligands coordinated in bidentate manner.

ACKNOWLEDGEMENT

We thank the School of Chemical Sciences and Food Technology, UKM for the provision of laboratory facilities and technical assistance. The authors also gratefully acknowledge the research grant from IRPA 09-02-02-0048-EA144 and scholarship for Indah Raya from TPSDP Hasanuddin University Indonesia for the Doctor of Philosophy (PhD) degree.

REFERENCES

Bellamy, L.J. 1975. The Infrared Spectra of Complex Molecules. London: Chapman and Hall.

Brown, D.A., Glass, W.K. & Burke, M.A. 1976. The General Use of IR Spectral Criteria in Disscussions of the Bonding and Structure of Metal Dithiocarbamate. *Spectrochem. Acta* 32A:137-143.

Coucouvanis, D. & Fackler, J. P. Jr. 1976. Square-planar sulphur complexes. *Inorganic Chem.* 6: 2047-2053.

Criado, J.J., Fernandez, I. & Macias, B. 1990. Novel Chelates of Pd(II) Dithiocarbamates, Spectroscopic Studies and Thermal Behaviour. *Inorg. Chem. Acta* 174:67-75.

Haas, W. & Schwarz, T. 1963. NH_4 Diethanol Dithiocarbamate a Reagent for the Spectrophotometric Determination of Mo and U. *Microchem. Ichonal. Acta* 58: 253-259.

Hursthouse, M. B., Malik, M. A., Motervalli, M. & O'Brien, P. 1992. The Crystal and Molecular Structure of N,N-dim ethyldiselenocarbamatocadmium(II): Cadmium and Zinc Dimethyldiselenocarbamates as Precursors for Selenides. *Polyhedron* 11: 45-48.

Indah Raya, Ibrahim Baba, Bohari Mohd Yamin & Djulia Onggo. 2007. Ganolinium(III) Complexes with Dialkyldithiocarbamates and 1,10-Phenanthroline. *Sains Malaysiana* 36(1): 15-20.

Nomura, R., Takabe, A., & Matsuda, H. 1987. Facile Synthesis of Antimony Dithiocarbamate Complexes. *Polyhedron* 6: 411-416.

Sheldrick, G.M. 1996. SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany.

Sheldrick, G.M. 1997. SHELXTL V 5.1, Software Reference Manual, Bruker AXS, Inc., Madison, WI, USA.

Siddal, T.H. & Steward, W.E. 1970. Preparation and Studies of Magnetic and Spectroscopic Properties of Alkyl Ammonium Lanthanide Tetrakis (N,N-dialkyldithiocarbamates). *J. Inorg Nuclear Chem.* 32: 1147-1158.

Siemens, 1996, *SMART* and *SAINT*. Area Detector Control and Integration Software. Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA.

Su,C.,Tan,M.,Tang,N.,Gan,X.&Liu,W. 1997.Synthesis,Structure and Spectroscopic Properties of Dimmethylammonium Lanthanide Tetrakis(*N*, *N*-dimmethyldithiocarbamate). *Polyhedron* 16: 1643-1650.

Tang, N., Zhu, H., Tan, M., Gan, X. & Wang, A. 1991. Synthesis and Characterisation of Dimethylammonium Lanthanide (monomethyldithiocarbamate). *Polyhedron* 16: 1643-1650.

Thorn, G.D. & Ludwig, R.A. 1962. *The Dithiocarbamates and Related Compounds*. New York: Elsevier Pub. Co.

Zhu, H., Tang, N., Gan, X., Wang, A. & Tan, M. 1993. Synthesis and Characterization of Light Lanthanide Piperidinocarbodithioate Complexes. *Polyhedron* 12: 945-991.

School of Chemical Sciences & Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor D. E.
MALAYSIA

Received: 4 April 2008
Accepted: 4 August 2008

Synthesis and structural studies of lanthanum (Iii) Dialkyldithiocarbamates 1, 10-phenanthroline

ORIGINALITY REPORT

18%	11%	13%	7%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Choi, K.S.. "Eightfold Superstructure in K"2Gd"2Sb"2Se"9 and K"2La"2Sb"2S"9 Caused by Three-Dimensional Ordering of the 5s^2 Lone Pair of Sb^3^+ Ions", Journal of Solid State Chemistry, 199910 Publication	2%
2	Submitted to Higher Education Commission Pakistan Student Paper	1%
3	Submitted to National University of Singapore Student Paper	1%
4	hdl.handle.net Internet Source	1%
5	webdoc.sub.gwdg.de Internet Source	1%
6	S. Yokoyama. "Self-Organized (100)-/(001)-Preferred Orientation in Pb(Zr,Ti)O 3 Films Grown on Polycrystalline Substrates by	1%

	Metalorganic Chemical Vapor Deposition", Integrated Ferroelectrics, 06/01/2003 Publication	
7	Sun, C.Y.. "Supramolecular architectures from the self-assembly of lanthanide ions with 6-hydroxypicolinic acid and 1,10-phenanthroline", Journal of Molecular Structure, 20050502 Publication	1 %
8	www.sphinxsai.com Internet Source	1 %
9	www.ukm.my Internet Source	1 %
10	www.novusscientia.org Internet Source	1 %
11	hal.archives-ouvertes.fr Internet Source	1 %
12	Submitted to Universiti Kebangsaan Malaysia Student Paper	1 %
13	Submitted to Chulalongkorn University Student Paper	1 %
14	open.library.ubc.ca Internet Source	1 %
15	repository.ias.ac.in Internet Source	1 %

16	Khorasani-Motlagh, M.. "Lanthanum(III) complexes with phenylcyanamide ligands: Synthesis and crystal structure", Inorganica Chimica Acta, 20120330 Publication	<1 %
17	Michael A. Boreen, Bernard F. Parker, Stephan Hohloch, Brighton A. Skeel, John Arnold. " f-Block complexes of a -terphenyl dithiocarboxylate ligand ", Dalton Transactions, 2017 Publication	<1 %
18	id.123dok.com Internet Source	<1 %
19	Cario, L.. "Synthesis and Structure Determination of La"8Ti"1"0S"2"4O"4", Journal of Solid State Chemistry, 19980215 Publication	<1 %
20	Chew Hee Ng. "An oxido-bridged dinickel(II) complex with L-alanine derived spiro ligand from an unusual mannich aminomethylation", Journal of Coordination Chemistry, 11/10/2005 Publication	<1 %
21	Daike Li, Xinmin Gan, Minyu Tan, Xin Wang. "Synthesis and characterization of lanthanide complexes of 1,4,7,10,13-	<1 %

pentaazacyclopentadecane", Polyhedron, 1997
Publication

22	M. Sukeri M. Yusof, Bohari M. Yamin. "3-(3-Benzoylthioureido)propionic acid", Acta Crystallographica Section E Structure Reports Online, 2003 Publication	<1 %
23	Submitted to University of St Andrews Student Paper	<1 %
24	jyx.jyu.fi Internet Source	<1 %
25	bsj.uobaghdad.edu.iq Internet Source	<1 %
26	Adeyemo, A.O.. "Mercury(II) complexes of vitamin B"1", Inorganica Chimica Acta, 19890615 Publication	<1 %
27	Indah Raya, Ibrahim Baba, Fatimatul Z. Rosli, Bohari M. Yamin. " Bis(-isopropyl- -phenylthiocarbamoyl) disulfide ", Acta Crystallographica Section E Structure Reports Online, 2005 Publication	<1 %
28	Noss, H.. "Concerning the question of f- and d-electron interactions in heterodinuclear compounds: synthesis, structure and	<1 %

^1^0^3Rh NMR investigations of La@?Rh-bimetallics", Inorganica Chimica Acta, 20030310
Publication

29 Senthilkumar Balakrishnan, Senbagam Duraisamy, Murugan Kasi, Selvam Kandasamy, Rajesh Sarkar, Anbarasu Kumarasamy. "Syntheses, physicochemical characterization, antibacterial studies on potassium morpholine dithiocarbamate nickel (II), copper (II) metal complexes and their ligands", Heliyon, 2019 <1 %
Publication

30 Jorge Cruz-Huerta, Manuel Carillo-Morales, Ericka Santacruz-Juárez, Irán F. Hernández-Ahuactzi et al. "Macrocyclic Diorganotin Complexes of γ-Amino Acid Dithiocarbamates as Hosts for Ion-Pair Recognition", Inorganic Chemistry, 2008 <1 %
Publication

Exclude quotes	On	Exclude matches	< 5 words
Exclude bibliography	On		