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Organic-inorganic hybrid complexes of Lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids

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A new set of organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids of composition $Pb[RC(O)\overbrace{C:C(O)N(C_6H_5)N:C}CCH_3][\overbrace{C(O)C_6H_4C(O)}NCHR'COO]$ (where R = C_6H_5, p-ClC_6H_4, CH_3 and R' = $CH(CH_3)C_2H_5$, $CH_2CH(CH_3)_2$ and $CH(CH_3)_2$) has been generated by the reactions of freshly prepared lead isopropoxide with sterically demanding heterocyclic β-diketones (LH) and flexible N-protected amino acids (AH) in 1:1:1 molar ratio in refluxing dry benzene . These lead(II) complexes of mixed organic ligands have been characterized on the basis of physico-chemical and spectroscopic studies.

Keywords: Lead(II) isopropoxide, Heterocyclic β-diketones, N-protected amino acids, Distorted trigonal bipyramidal geometry

The role of the concept of mixed organic ligands in the design of organic-inorganic hybrid complexes is an active area of research and is developing at rapid pace due to its applicability and properties[1-4]. The construction of organic-inorganic hybrid materials results in the development of interesting framework structures and various applications[5-7]. Metal-organic frameworks have interesting molecular architectures and find potential applications in functional materials[8-9], molecular magnetic materials[10], electrical conductivity[11], ion exchange[12], non-linear optics[13,14], luminescence[15], and specific catalysis[15,16].

Lead is ubiquitous and is used in various industries like batteries[17,18], ceramics[19-21] and paints[22,23]. Due to this, the occurrence of lead in the environment and biological systems has increased manifold. Lead toxicity[24,25] and lead poisoning[26-29] are highly explored and well-documented topics. The developmental toxicity associated with lead poisoning may be due to the interaction of lead(II) with proteins containing thiol rich structural zinc binding sites. Lead(II) is known to bind in a three coordinate Pb(II)-S_3 mode in these proteins consistent with a trigonal pyramidal Pb(II)-S_3 geometry which is different from the four coordinate mode of zinc in these sites. Thus, the structure of these peptides is altered by lead.

The large size of lead and its 6s electron pair are important factors in the coordination chemistry of lead(II). Its 6s electron pair may be active or inactive[30,31]. Both soft and hard donor atom ligands react with lead(II) ions to form stable complexes[32].

Lead toxicity is insidious health hazard to humans. There is significant increase in the amount of lead released into the natural environment. Hence, it is pertinent to devise strategy for the removal of this toxic metal lead from the human body using potential chelating agents. A number of chelating agents have been designed in the therapy of lead poisoning[33,34]. Sterically demanding heterocyclic β-diketones and flexible N-protected amino acids are important chelating agents. In view of the interesting results obtained in our previous communication related to the interaction of heterocyclic β-diketones with simple lead(II) isopropoxide[35], we now report the interaction of two different classes of chelating agents such as heterocyclic β-diketones and flexible N-protected amino acids with freshly prepared lead(II) isopropoxide. This interaction resulted in the formation of stable organic-inorganic hybrid complexes of lead in subvalent state. Thus, the present study of the interaction of lead(II) isopropoxide with heterocyclic β-diketones and flexible N-protected amino acids gives insights into the understanding of the possible chelation therapy of lead poisoning[36,37].

Materials and Methods

All the chemical reactions were carried out under strictly anhydrous conditions. Lead isopropoxide was

prepared by reported method[38]. The organic ligands, sterically demanding heterocyclic β-diketones and N-protected amino acids were synthesized by reported methods[39,40]. The solvents were dried by standard methods[41]. Lead was estimated as lead chromate[41]. IR (4000-400 cm^{-1}) spectra were recorded on FTIR spectrophotometer using SHIMADZU Japan 8400s and samples were prepared as KBr pellets. ^{1}H and ^{13}C NMR spectra of the samples were recorded in DMSO-d_6 on BRUKER AVANCE II 400 NMR spectrometer. Mass spectra were recorded on Waters Mass Spectrometer.

Synthesis of organic-inorganic hybrid complexes of lead(II)

A similar method was used for the synthesis of all these Pb(II) complexes of sterically demanding heterocyclic β-diketones and N-protected amino acids. The preparation of one representative complex is described and the results of other complexes are given in Table 1.

Preparation of complex 1, Pb(L1)(A1)

Pb(II)[$C_6H_5C(O)\overline{C:C(O)N(C_6H_5)N:CCH_3}$][$\overline{C(O)C_6H_4C(O)N}$CHCH($CH_3$)$C_2H_5$COO]

The two organic ligands, sterically demanding heterocyclic β-diketones (4-benzoyl-2,4-dihydro-5-methyl-2phenyl-3H-pyrazole-3-one, L_1H) (0.75 mmol, 0.21 g) and N-protected amino acids (N-phthaloyl isoleucine, A_1H) (0.75 mmol, 0.19 g) were dissolved in dry benzene and then were added to a dry benzene solution of freshly prepared lead isopropoxide (0.75 mmol, 0.24 g). The reaction contents were refluxed for about 8 h. The liberated isopropanol in the azeotrope was estimated by oxidimetric method to monitor the progress of the reaction. The excess solvent was removed under reduced pressure and subsequently, a white solid product was obtained. The product was purified by washing with n-hexane. The physical and analytical data of the complexes are given in Table 1.

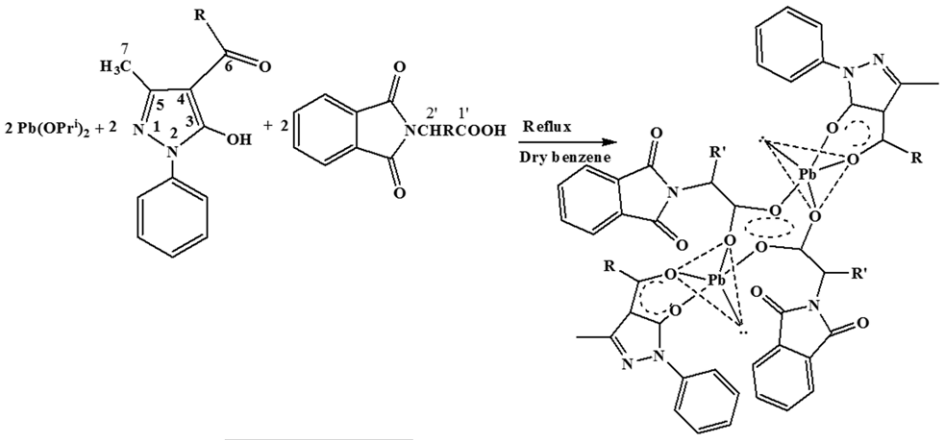
Results and Discussion

Some new organic-inorganic hybrid complexes of lead(II) having the general formula PbLA (where LH=heterocyclic β-diketones and AH = N-protected amino acids) were generated by the interaction of freshly prepared lead(II) isopropoxide with two different chelating agents such as sterically demanding heterocyclic β-diketones (LH) and flexible N-protected amino acids (AH) in 1:1:1 molar ratio in refluxing dry benzene (Scheme 1).

Isopropanol liberated in these reactions was fractionated off azeotropically with benzene. The liberated isopropanol in the azeotrope was estimated to monitor the progress of the reaction. The excess solvent was removed under reduced pressure. After this, organic-inorganic hybrid complexes of Pb(II) were obtained. These solid products were purified by washing with dry benzene. These white to light yellow coloured solids are sparingly soluble in common organic solvents like benzene, THF, chloroform but are soluble in dimethylsulphoxide. These complexes decompose on heating. The physical properties of these products are given in Table 1.

Table 1 — Physical and analytical data of Pb(II) complexes of sterically demanding heterocyclic β-diketones and N-protected amino acids

Complex No.	Product formula (empirical formula)	Reagents in g (mmol)			Pr^iOH in g found (calc.)	Colour	% Yield	% Pb found (calc.)	% C found (calc.)	% H found (calc.)	% N found (calc.)
		LH	AH	$Pb(OPr^i)_2$							
1	Pb(L1)(A1)	0.21	0.19	0.24	0.08	White	84	27.80	50.00	3.64	5.62
	($C_{31}H_{27}N_3O_6Pb$)	(0.75)	(0.75)	(0.75)	(0.09)			(27.82)	(49.99)	(3.65)	(5.64)
2	Pb(L2)(A1)	0.24	0.20	0.25	0.08	White	81	26.58	47.75	3.37	5.40
	($C_{31}H_{26}N_3O_6ClPb$)	(0.78)	(0.78)	(0.78)	(0.09)			(26.59)	(47.78)	(3.36)	(5.39)
3	Pb(L3)(A1)	0.22	0.26	0.33	0.12	Light	75	30.34	45.76	3.67	6.16
	($C_{26}H_{25}N_3O_6Pb$)	(1.02)	(1.02)	(1.02)	(0.12)	yellow		(30.35)	(45.74)	(3.69)	(6.15)
4	Pb(L1)(A2)	0.22	0.20	0.26	0.08	white	85	27.81	49.97	3.66	5.66
	($C_{31}H_{27}N_3O_6Pb$)	(0.80)	(0.80)	(0.80)	(0.09)			(27.82)	(49.99)	(3.65)	(5.64)
5	Pb(L2)(A2)	0.33	0.27	0.34	0.11	white	79	26.57	47.79	3.34	5.38
	($C_{31}H_{26}N_3O_6ClPb$)	(1.05)	(1.05)	(1.05)	(0.12)			(26.59)	(47.78)	(3.36)	(5.39)
6	Pb(L3)(A2)	0.41	0.50	0.43	0.22	Light	74	30.33	45.72	3.70	6.15
	($C_{26}H_{25}N_3O_6Pb$)	(1.91)	(1.91)	(1.91)	(0.22)	yellow		(30.35)	(45.74)	(3.69)	(6.15)
7	Pb(L1)(A3)	0.29	0.26	0.34	0.12	white	82	28.34	49.31	3.42	5.73
	($C_{30}H_{25}N_3O_6Pb$)	(1.04)	(1.04)	(1.04)	(0.12)			(28.35)	(49.30)	(3.44)	(5.75)
8	Pb(L2)(A3)	0.17	0.20	0.18	0.08	Light	81	27.06	47.05	3.18	5.50
	($C_{30}H_{24}N_3O_6ClPb$)	(0.55)	(0.55)	(0.55)	(0.06)	yellow		(27.07)	(47.08)	(3.16)	(5.49)
9	Pb(L3)(A3)	0.91	1.04	1.37	0.49	Light	72	30.95 (	44.91	3.45	6.26
	($C_{25}H_{23}N_3O_6Pb$)	(4.22)	(4.22)	(4.22)	(0.50)	yellow		30.98)	(44.90)	(3.46)	(6.28)



Where, LH = $RCOC{:}C(OH)N(C_6H_5)N{:}CCH_3$

$R = C_6H_5$ (L1H), $R = p\text{-}ClC_6H_4$ (L2H), $R = CH_3$ (L3H)

AH = $C(O)C_6H_4C(O)NCHR'COOH$

R' = $CH(CH_3)C_2H_5$ (A1H), R' = $CH_2CH(CH_3)_2$ (A2H), R' = $CH(CH_3)_2$ (A3H)

$R = C_6H_5$	R' = $CH(CH_3)C_2H_5$	Pb(L1) (A1)	Complex **1**
R = p-(Cl)C_6H_4	R' = $CH(CH_3)C_2H_5$	Pb(L2)(A1)	Complex **2**
$R = CH_3$	R' = $CH(CH_3)C_2H_5$	Pb(L3) (A1)	Complex **3**
$R = C_6H_5$	R' = $CH_2CH(CH_3)_2$	Pb(L1) (A2)	Complex **4**
R = p-(Cl)C_6H_4	R' = $CH_2CH(CH_3)_2$	Pb(L2)(A2)	Complex **5**
$R = CH_3$	R' = $CH_2CH(CH_3)_2$	Pb(L3)(A2)	Complex **6**
$R = C_6H_5$	R' = $CH(CH_3)_2$	Pb(L1)(A3)	Complex **7**
R = p-(Cl)C_6H_4	R' = $CH(CH_3)_2$	Pb(L2)(A3)	Complex **8**
$R = CH_3$	R' = $CH(CH_3)_2$	Pb(L3) (A3)	Complex **9**

Scheme 1 — Schematic representation for the generation of organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids

IR Spectra

The IR spectra of some representative organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids were recorded in KBr pellets in the region 4000-400 cm^{-1}.

The IR spectra of these lead(II) complexes exhibit new medium intensity bands in the region 476-409 cm^{-1} which may be due to the formation of Pb-O bonds[32]. The IR spectra of sterically demanding heterocyclic β-diketones exhibit a band at ~ 1545 cm^{-1} which may be assigned to ν(>C=O) stretching[7]. This band shifts to a lower wavenumber in the IR spectra of the complexes. This observation supports the bidentate nature of sterically demanding heterocyclic β-diketones. The absorption bands present in the region ~ 1555 cm^{-1} and 1590-1600 cm^{-1} may be attributed to ν(>C=C</>C=N-) and ν(Ph) stretching vibrations, respectively[1,35].

N-Protected amino acids are also involved in the formation of these organic-inorganic hybrid complexes of lead(II). In the IR spectra of N-protected amino acids, the bands observed in the region 1770±5 cm^{-1} and ~ 1400 cm^{-1} may be attributed to $\nu(CO)_{asym}$ and $\nu(COO)_{sym}$ vibrations, respectively[1] and remained unchanged after complexation. A broad band in the region 1700-1730 cm^{-1} appeared in the IR spectra of N-protected amino acids which may be due to the merger of $\nu(CO)_{sym}$ and $\nu(COO)_{asym}$ bands[1]. These bands split after complexation. In the IR spectra of lead(II) complexes, $\nu(CO)_{sym}$ and $\nu(COO)_{asym}$ bands were observed in the regions 1709-1717 cm^{-1} and 1565-1580 cm^{-1}, respectively. The Δν value ($\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}$) calculated for these complexes was in the range of 177-193 cm^{-1} which reveals the bridging bidentate chelation of N-protected amino acids in these Pb(II) complexes[42].

NMR Spectra

The ^1H NMR spectra of these organic-inorganic hybrid complexes of lead(II) were recorded in DMSO-d_6 solution using TMS as an internal reference and are summarized in Table 2. The carboxylic –OH protons of N-protected amino acids and enolic –OH protons of sterically demanding heterocyclic β-diketones appeared in the regions of δ 8.90-10.62 and δ 11.25-11.51, respectively[1]. The disappearance

Table 2 — ^{1}H NMR spectra of Pb(II) complexes of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids

Complex no.	Ligands & Complexes	RCOC:C(OH)N(C_6H_5)N:CCH$_3$ (LH)						$C(O)C_6H_4C(O)NCHR'COOH$ (AH)				
		OH	Ring CH_3	Ring Ph	Terminal			COOH	C_6H_4	CH	CH_2	CH_3
					C_6H_5	p-ClC_6H_4	CH_3					
	A1H							10.62 (bs)	7.28-7.88 (m)	4.76 (d, *J*=7.7Hz), 2.55 (m)	1.52 (m)	0.82 (t, *J*=7.2Hz), 1.12 (d, *J*=6.6Hz)
	L1H[a]	11.25 (bs)	2.10 (s)	7.25-7.89 (m)	*							
1	Pb(L1)(A1)	-	1.58 (s)	7.04-8.25 (m)	*			-	*	4.26 (d, *J*=9.04 Hz) 2.50(m)	1.44 (m)	0.86 (*J*=7.7Hz) 1.09(*J*=6.7 Hz)
	(L2) H[a]	11.37 (bs)	2.14 (s)	7.26-8.00 (m)		*						
2	Pb(L2 (A1)	-	1.74 (s)	7.04-8.23 (m)		*		-	*	4.26 (d, *J*=9.04 Hz) 2.51(m)	1.45 (m)	0.85(*J*=7.8 Hz) 1.09 (*J*=6.6 Hz)
	(L3) H[a]	11.51 (bs)	2.51 (s)	7.17-7.83 (m)			2.45 (s)					
3	Pb(L3)(A1)	-	2.16 (s)	7.17-8.15 (m)			2.21 (s)	-	*	4.21 (d, *J*=9.08 Hz) 2.45(m)	1.40 (m)	0.73(*J*=7.4 Hz) 1.08(*J*=6.7 Hz)
	A2 H							10.32 (bs)	7.27-7.87 (m)	4.99 (t, *J*=7.1 Hz), 2.39 (m)	1.50 (m)	0.91(s), 0.95 (s)
4	Pb(L1)(A2)	-	1.61 (s)	7.07-8.25 (m)	*			-	*	4.60(*J*=7.6 Hz) 2.34 (m)	1.49 (m)	0.87, 0.86
5	Pb(L2)(A2)	-	1.75 (s)	7.02-8.26 (m)		*		-	*	4.57(*J*=7.6 Hz) 2.30(m)	1.45 (m)	0.87, 0.86
6	Pb(L3)(A2)	-	1.92 (s)	7.04-8.22 (m)			2.21 (s)	-	*	4.57(*J*=7.6 Hz) 2.31(m)	1.45 (m)	0.87, 0.88
	A3H							08.90 (bs)	7.28-7.89 (m)	4.63 (d , *J*=8.4 Hz), 2.76 (m)		1.17 (d,*J*=6.8Hz), 0.90 (d, *J*=6.8 Hz)
7	Pb(L1)(A3)	-	1.58 (s)	7.15-7.98 (m)	*			-	*	4.43 (d, *J*=8.4 Hz) 2.56(m)		0.86(*J*=6.7 Hz) 1.15 (*J*=6.7 Hz)
8	Pb(L2)(A3)	-	1.90 (s)	7.26-8.16 (m)		*		-	*	4.23 (d, *J*=8.8 Hz) 2.56(m)		0.85(*J*=6.8 Hz) 1.16(*J*=6.8 Hz)
9	Pb(L3)(A3)	-	2.10 (s)	7.27-8.22 (m)			2.22 (s)	-	*	4.17 (d, *J*=8.7 Hz) 2.52(m)		0.85(*J*=6.6 Hz) 1.17(*J*=6.6 Hz)

*=signal merged in phenyl region, a= ref.no.7, bs=broad singlet, s=singlet, m=multiplet, d=doublet

of these signals in the ^{1}H NMR spectra of Pb(II) complexes indicates deprotonation of these ligands and formation of Pb-O bonds[35]. A complex pattern of signals was observed in the region δ 7.02-8.26 which may be due to aromatic protons of sterically demanding heterocyclic β-diketones in lead(II) complexes. Aromatic protons of N-protected amino acids are overlapping with the above mentioned complex pattern of signals. Aliphatic protons of N-protected amino acids and sterically demanding heterocyclic β-diketones present in lead(II) complexes appeared in the region δ 0.73-4.60[42].

^{13}C NMR Spectra

The ^{13}C NMR spectra of organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids were recorded in DMSO-d_6 solution using TMS as an internal reference and are summarized in Table 3. It is of interest to study the comparative coordination propensity of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids towards Pb(II). In the ^{13}C NMR spectra of Pb(II) complexes, there are some shifts in the positions of C_3, C_4 and C_6 carbon signals of sterically demanding heterocyclic β-diketones which may be due to the formation of quasi-aromatic ring and delocalization of electrons in it. This indicates the bidentate nature of sterically demanding heterocyclic β-diketones in Pb(II) complexes. The carboxylic carbon signal shows a downfield shift after complexation as compared to its position in the free ligands. This suggests bidentate chelation of carboxylic group of N-protected amino acids with central lead atom. Imido carbon signal appeared in the region δ 167.71-167.87 in the free N-protected amino acids. This group is not involved in bonding as there is no shift in its position in Pb(II) complexes.

Table 3 — ^{13}C NMR spectra of Pb(II) complexes of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids

Complex No.	Complex formula	RCOC:C(OH)N(C_6H_5)N:CCH$_3$ (LH)							C(O)C_6H_4C(O)NCHR'COOH (AH)					
		Terminal		Ring C_6H_5	C_3	C_4	C_5	C_6	C_7	COO	CO	CH_3	CH_2	CH	C_6H_4
		CH_3	C_6H_5/pClC_6H_4												
	A1H									174.61	167.80	10.90, 16.80	25.82	34.33, 56.97 (CH-N)	123.65, 131.59, 134.29
	L1H		137.17, 131.90, 128.42, 126.71	147.97, 129.13, 127.88, 120.77	161.43	103.58	137.57	192.04	15.82						
1	Pb(L1)(A1)		*	147.81-119.35	163.74	104.93	*	189.44	16.32	174.39	167.85	10.48 17.29	26.05	33.36 62.00	*
	L2H		137.05, 136.12, 131.52, 128.81	147.69, 129.38, 126.90, 120.90	161.07	103.46	138.23	191.23	15.90						
2	Pb(L2)(A1)		*	147.80-119.03	163.99	104.60	*	187.48	16.54	174.45	167.83	10.47 17.26	26.04	33.34 62.04	*
	A2H									175.79	167.71	23.09, 25.09	36.99	50.44 (CH-N)	123.61, 131.71, 134.26
4	Pb(L1)(A2)		*	147.72-119.46	163.66	105.10	*	189.57	16.27	174.93	167.86	25.08 23.13	36.95	55.44	*
5	Pb(L2)(A2)		*	147.80-118.99	164.04	104.50	*	187.45	16.58	174.88	167.91	25.08 23.14	36.93	55.45	*
	A3H									173.82	167.87	19.46, 20.94		28.42, 57.49 (CH-N)	123.64, 131.53, 134.52
7	Pb(L2)(A3)		*	147.80-118.87	164.14	104.50	*	187.50	16.61	174.22	167.80	20.25 21.58		27.65 62.83	*
	L3H	26.66		147.69, 129.11, 126.60, 120.67	160.40	104.23	137.19	194.40	15.57						
8	Pb(L3)(A3)	28.03		147.52-119.48	161.09	105.00	*	191.15	17.08	174.37	167.73	20.22 21.49		27.65 62.96	*

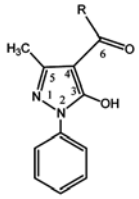
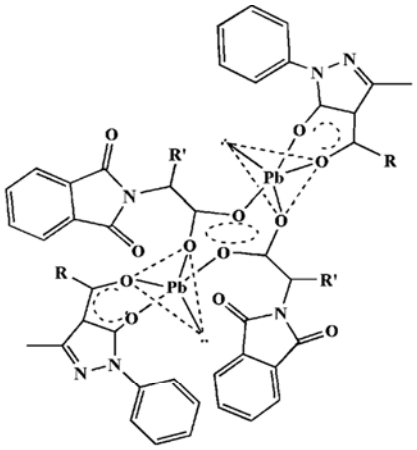


Table 4 — Mass spectra of Pb(II) complexes of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids

Complex No.	2M*	2M-R	2M-$C_8H_4NO_2$-y	2M- $C_8H_4O_2$-x	2M-L/A-z	M/M±1/ M±2	M-R	M- $C_8H_4NO_2$-Y	M- $C_8H_4O_2$-X	M-L/A-Z	Other low value ion
1	1489	1479 (R=CH_3) 1309 (R=2Ph+2CH_3)		1196 (x=$C_8H_4O_2$+2CH_3);	1230 (2M-L); 1213 (2M-A); 1039(2M-L-$C_8H_4NO_2$-C_2H_5) 864(2M-L-Bu-Me); 763(2M-A-$C_8H_4NO_2$-C_3H_8)	745, 746, 744		555 (Y=3CH_3); 284 ($C_8H_4NO_2$-2Ph-CH_3)	397 (X= 2Ph-3 CH_3)	485 (M-A)	160 ($C_8H_4N(O)_2$-CH)
2	1558		1196 (y=$C_8H_4NO_2$+C_5H_{10})		1247 (2M-L)					519 (M-A) 468 (M-L) 423 (M-L-3CH_3)	208(Pb)
4	1489	1478 (R=CH_3)		1196 (x=$C_8H_4O_2$+2CH_3);	1213 (2M-L);" 1067(2M-L-$C_8H_4NO_2$); 1048 (2M-L-Bu-Ph-2CH_3); 768(2M-L-2Ph-2$C_8H_4NO_2$); 750 (2M-L-A-Bu-$C_8H_4NO_2$)	589 (R=2Ph)		433 (Y=Ph+$C_6H_5N_2$ +CH_3+Pr^i)		485(M-A) 405 (M-L-Ph)	331 [Pb(COO)(C_4O_2)] 186(LH-C_6H_5N) 175 ($C_8H_4N(O)_2$-CH CH_2)
6	1365		1219(y=0); 1018(y=$C_8H_4O_2$+C_5H_{10}) 986(y=$C_8H_4O_2$+C_5H_{10}+2CH_3) 961(y=$C_8H_4NO_2$+2Bu)	1154 (x=Ph);	833(2M-L-A-Bu); 739 (2M-L-A-Bu-Ph-CH_3)	549 (R=Ph+Bu)			533 (X=0); 481 (X=Bu)	454 (M-L-CH_3) 408 (M-A-CH_3); 302 (M-A-Ph-3CH_3)	213 (L); 207 (Pb)
8	1530							582(Y=Cl); 533(Y=Bu^i+2CH_3); 465(Y=PhCl+Pr^i)		393(M-A-PhCl-Me)	313 (LH)
9	1337	1228 (R=Ph+2Me)	1192 (y=0)					521(Y=0); 466(Y= Bu^i)		422 (M-A)	207 (Pb)

Mass Spectra

ESI-mass spectra of some representative lead(II) complexes were recorded. Their fragmentation and m/z values are given in Table 4. Molecular ion peak of the complexes was rarely observed. Isotopic peaks for various fragments are observed in the mass spectra of organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and



R = C_6H_5	R' = $CH(CH_3)C_2H_5$	Pb(L1) (A1)	Complex 1
R = p-(Cl)C_6H_4	R' = $CH(CH_3)C_2H_5$	Pb(L2)(A1)	Complex 2
R = CH_3	R' = $CH(CH_3)C_2H_5$	Pb(L3) (A1)	Complex 3
R = C_6H_5	R' = $CH_2CH(CH_3)_2$	Pb(L1) (A2)	Complex 4
R = p-(Cl)C_6H_4	R' = $CH_2CH(CH_3)_2$	Pb(L2)(A2)	Complex 5
R = CH_3	R' = $CH_2CH(CH_3)_2$	Pb(L3)(A2)	Complex 6
R = C_6H_5	R' = $CH(CH_3)_2$	Pb(L1)(A3)	Complex 7
R = p-(Cl)C_6H_4	R' = $CH(CH_3)_2$	Pb(L2)(A3)	Complex 8
R = CH_3	R' = $CH(CH_3)_2$	Pb(L3) (A3)	Complex 9

Fig. 1 — Proposed structure of lead(II) complexes

flexible N-protected amino acids. The peaks appeared due to the fragmentation of dimeric as well as monomeric complexes which supports the formation of dimeric complexes. Molecular ion peak was not observed for dimeric state as well as for monomeric state except complex 1.

The crystal structure of Pb(II) complex of sterically demanding heterocyclic β-diketone of composition $Pb(II)[CH_3C(O)C{:}C(O)N(C_6H_5)N{:}CCH_3]_2$ has been reported in our previous communication[35]. Three molecules are present in an asymmetrical unit. Two crystallographically equivalent heterocyclic β-diketone ligands are chelating each central lead atom. The stereochemical implications of lone pair present on lead in this complex were studied which lead to angular distortions. As a consequence of distortions, a distorted trigonal bipyramidal geometry was assigned to this complex. In this geometry, an equatorial position was occupied by the lone pair of electrons.

Similarly, the geometry of these organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids may be suggested as distorted trigonal bipyramidal with the lone pair of electrons occupying an equatorial position. On the basis of physico-chemical and spectroscopic evidences, the following plausible structure may be suggested for Pb(II) complexes as shown in Fig. 1. These lead(II) complexes contain tetracoordinated lead centres. The sterically demanding heterocyclic β-diketones are behaving as bidentate ligands whereas N-protected amino acids act as bridging bidentate chelating agents. Each central lead atom is surrounded by four oxygen atoms in these metallacyclic systems. These complexes possess one eight membered ring and two six membered rings.

Conclusions

Organic-inorganic hybrid complexes of lead(II) of sterically demanding heterocyclic β-diketones and flexible N-protected amino acids were generated and characterized spectroscopically. A distorted trigonal bipyramidal geometry with the lone pair of electrons occupying an equatorial position was suggested for these organic-inorganic hybrid complexes of lead(II).

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(02)202-208_SupplData.pdf.

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