Complexes of Organometallic Compounds. XXVII.

Studies on Diorganolead(IV) Moieties Six-coordinated by ONNO Tetradentate Ligands

By F. Di Bianca, E. Rivarola, G. C. Stocco and R. Barbieri.

Abstract. New complexes R_2PbL, where L^{2-} are the dianions, in the "planar" Schiff base form, of the tetradentate ONNO ligands α, α′ (ethylenedinitrilo)dicresol and 2,2′ bis-benzoxazoline, were synthesized. Their configuration was investigated at the solid state by infrared spectroscopy, and in solution phase mainly by electronic and PMR spectroscopy. An octahedral type structure with linear CPbC moieties, and the ONNO ligand atoms chelating Pb^{IV} in a square plane, was advanced.

Inhaltsübersicht. Darstellung neuer Komplexverbindungen: R_2PbL ($R = CH_3$, C_2H_5, C_6H_5; L^{-2} sind zweiwertige Anionen, in der „planaren" Schiffschen Basen-Konfiguration, der vierzähnigen ONNO-Liganden Disalicylal-äthylendiamin und Glyoxal-bis-[2-hydrocyanil]).

In festem Zustand wurden die Strukturen durch IR-Spektren und in Lösung durch ^{1}HMR- und Elektronenspektren untersucht, und es wird eine oktaedrische Struktur mit einem linearen R_2Pb-Rest und den ONNO-Atomen mit einer vierzähligen planaren Anordnung um das Blei-(IV)-Atom vorgeschlagen.

In diorganolead(IV) salts and complexes, it appears that R_2Pb^{IV} moieties prefer a linear configuration, as shown by the few researches on the structural chemistry of diorganolead(IV) derivatives up-to-date reported in the literature. Diphenyllead dichloride has a polymeric crystal structure, Pb^{IV} atoms being six-coordinated, with four bridging chlorides located in the square plane and a linear, "quasi" perpendicular, CPbC skeleton¹). The same configuration was inferred by vibrational spectroscopic studies for solid R_2Pbhal_2,²⁻⁴) while solid $Me_2Pb(acetylacetonate)_2$ and $Ph_2Pb(NCS)_4^{2-}$

---

¹) M. Mammi, V. Busetti and A. Del Pra, Inorg. chim. Acta, 1, 419 (1967).

²) R. J. H. Clark, A. G. Davies and R. J. Puddephatt, J. Amer. chem. Soc., 90, 6923 (1968).

³) R. J. H. Clark, A. G. Davies and R. J. Puddephatt, Inorg. Chem. [Washington] 8, 457 (1969).

seem to show octahedral type structures with linear CPbC moieties[5][6]. Linear Me_2Pb^{IV} is believed to occur in a number of derivatives in solution phases [7][8]. Reported bent CPbC structures are much more limited. Examples are $Me_2PbPy_2(ClO_4)_2$[4] (where the 465 cm^{-1} vibrational band, assigned to $\nu_{as}(PbC_2)$[4], may be instead attributed to $\nu_s(PbC_2)$[2]), and R_2Pb^{IV} complexes with planar tridentate bases[9]. On the other hand, a bent CPbC configuration cannot be excluded on "a priori" grounds where structural studies are not available, such as in R_2Pb^{IV} coordination compounds (which indeed have been investigated at a very limited extent[10]). It may be predicted for $Ph_2Pbhal_3^-$ and R_2Pb halide oxinate[11][12], on the ground of the rules stated by Bent[13] and Muettertíes and Schunn[14], and perhaps for Ph_2Pb oxinate$_2$[15] and related compounds, taking into account the peculiar chelating behaviour of the oxinate ligand[16]. On the other hand, Me_2Pb oxinate$_2$ was assumed to contain a linear CPbC skeleton by PMR studies[8].

Model molecules for trigonal bipyramidal five-coordinated diorganolead(IV), where the CPbC moieties are very probably located in the trigonal plane, were previously synthesized and studied[9]. This paper reports successive studies on model molecules for six-coordinated diorganolead(IV) with a linear CPbC configuration. New complexes R_2PbL, where L^{2-} is the dianion of tetradentate bases with ONNO donor atoms, were prepared and structurally investigated by spectroscopic techniques. The ligands α,α'(ethylenedinitrilo)dicresol[17] (H_2Salen) and 2,2'bis-benzoxazoline[18–20] (H_2Gbha) were selected, which very probably act as "planar" tetraden-

---

[4] G. D. Shier and R. S. Drago, J. organometallic Chem. [Amsterdam] **6**, 359 (1966).

[5] N. Bertazzi and R. Barbieri, II° Convegno Naz. Chim. Inorg. Bressanone, 20—23 luglio 1969. p. 103 of the Abstracts; N. Bertazzi, G. Alonzo, A. Silvestri and G. Consiglio, to be published.

[6] Y. Kawasaki, T. Tanaka and R. Okawara, Bull. chem. Soc. Japan, **37**, 903 (1964).

[7] C. E. Freidline and R. S. Tobias, Inorg. Chem. [Washington] **5**, 354 (1966).

[8] Y. Kawasaki, J. organometallic Chem. [Amsterdam] **9**, 549 (1967); and Ref. therein.

[9] R. Bosco and R. Cefalù, J. organometallic Chem. [Amsterdam] **26**, 225 (1971).

[10] I. Ruidisch, H. Schmidbaur and H. Schumann, "Halogen Chemistry" vol. 2, p. 233. V. Gutmann Ed., Acad. Press., London—New York, 1967.

[11] F. Huber and E. Schönafinger, Angew. Chem. (Int. Ed.), **7**, 72 (1968).

[12] F. Huber and M. Enders, Z. Naturforsch. **20b**, 601 (1965).

[13] H. A. Bent, J. inorg. nuclear Chem., **19**, 43 (1961).

[14] E. L. Muettertíes and R. A. Schunn, Quart. Rev. (Chem. Soc. London), **20**, 245 (1966).

[15] G. Faraglia, L. Roncucci and R. Barbieri, Ric. Sci. Parte II, Sez. A **35**, 205 (1965).

[16] E. O. Schlemper, Inorg. Chem. [Washington] **6**, 2012 (1967).

[17] A. T. Mason, Ber. dtsch. chem. Ges., **20**, 267 (1887).

[18] E. Bayer, Chem. Ber., **90**, 2325 (1957).

[19] E. Bayer and G. Schenk, Chem. Ber., **93**, 1184 (1960).

[20] I. Murase, Bull. chem. Soc. Japan, **32**, 827 (1959).

tates in the dianion SCHIFF base form (see structures I and II under Discussion, this paper). A set of model molecules for five-coordinated diorganotin(IV)[21][22] and diorganolead(IV)[9], and for six-coordinated diorganotin(IV)[22] and diorganolead (IV), is thus now available.

Experimental

Analytical grade reagents and solvents (C. Erba, Milano) were used. Purification was attained, when necessary, through recrystallization or distillation, according to literature methods. The solvents were eventually dried by molecular sieves.

Tetramethyllead, tetraethyllead and diphenyllead dichloride were a gift from I. L. Z. R. O. through the Organic Chemistry Institute TNO, Utrecht. The dialkyllead dichlorides employed in this work were synthesized by literature methods[23], modified as follows.

a) Dimethyllead dichloride: About 60 mmole of tetramethyllead were slowly added under stirring to 250 ml of dry n-exane saturated with dry hydrogen chloride, at 0°C. Hydrogen chloride was then bubbled through the solution, under stirring, at 0°C, till the formation of flocculent trimethyllead chloride. The reaction mixture was allowed to attain room temperature, and dry chlorine was bubbled through, causing the formation of microcrystalline dimethyllead dichloride, which was recovered by cooling, filtering off, washing with anhydrous n-exane and ether, and drying under vacuum.

b) Diethyllead dichloride: About 50 mmole of tetraethyllead were added under stirring to about 170 ml of anhydrous toluene saturated with dry hydrogen chloride. The latter was then bubbled through the solution, at room temperature and under stirring, for about 15′. The progressive formation of diethyllead dichloride was checked by solubility tests on samples of the precipitate in boiling toluene, where the dichloride (but not triethyllead chloride) is insoluble. Diethyllead dichloride was then filtered off, washed with boiling toluene and dried under vacuum.

The dialkyllead dichlorides were stored in the dark at low temperature, to avoid decomposition.

The ligand α,α′(ethylenedinitrilo)dicresol[17], H_2Salen (usually indicated as N,N′-disalicylidene ethylenediimine), was prepared by condensation of 0.1 mole of ethylenediamine with 0.2 mole of salicylic aldehyde, in 100 ml of ethanol, recrystallized from 250 ml of ethanol and dried under vacuum. M. p.: 127°C (lit.[17]) 125—126°C). The ligand 2,2′ bis-benzoxazoline, H_2Gbha (usually indicated as glyoxal-bis-(2-hydroxyanil), being prepared by condensation of glyoxal with o-aminophenol[18–20])) was a product by Schuchardt, München.

The complexes Me_2PbL and Ph_2PbL (L^{2-} = $Salen^{2-}$ and $Gbha^{2-}$) were synthesized as follows.

The free ligands (5 mmole) were suspended in 200 ml of dry methanol, and reacted with 10 mmole of sodium metoxide in about 10 ml of methanol, at room temperature, thus obtaining solutions of the respective disodium salts. Insoluble impurities eventually present in $H_2 \cdot$ Gbha were filtered off. These solutions were then added under stirring, at room temperature, to 5 mmole of the diorganolead dichlorides suspended in 100—200 ml of dry methanol. Disso-

---

[21] R. CEFALÙ, R. BOSCO, F. BONATI, F. MAGGIO and R. BARBIERI, Z. anorg. allg. Chem., **376**, 180 (1970); and Ref. therein.

[22] R. H. HERBER and R. BARBIERI, Gazz. chim. ital. **101**, 149 (1971).

[23] R. W. LEEPER, L. SUMMERS and H. GILMAN, Chem. Reviews, **54**, 101 (1959); and Ref. therein.

lution took place, indicating complex formation, and the solid crystalline compounds slowly precipitated at room temperature.

Et_2PbL was prepared essentially by the above procedure, with the difference that a solution of diethyllead dichloride in 35 ml of dry methanol was added to the disodium salts dissolved in 60 ml of dry methanol; this owing to the greater solubility of Et_2Pb^{IV} derivatives.

The complexes were filtered off, washed with methanol and dried under vacuum on P_4O_{10}. The analytical data are reported in Table 1. The compounds are stable when stored in the dark and under anhydrous conditions. Their solubility is very poor in common organic solvents; as a consequence, the determination of molecular weigths by osmometry was not feasible.

Table 1

Analytical Data

		C%	H%	N%	O%	Pb%
Compound(a) (Colour)	m. p (°C)	Found (Calcd)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)
$Me_2PbSalen$ (yellow)	~196 (dec)	42.64 (42.93)	4.30 (4.00)	5.47 (5.56)	6.32 (6.36)	41.30 (41.15)
$Et_2PbSalen$ (yellow)	~158 (dec)	45.08 (45.18)	4.81 (4.55)	5.35 (5.27)	6.20 (6.02)	38.76 (38.98)
$Ph_2PbSalen$ (yellow)	~230 (dec)	53.70 (53.57)	3.94 (3.86)	4.66 (4.46)	5.27 (5.10)	33.24 (33.01)
$Me_2PbGbha$(b) (black)		40.15 (40.41)	3.33 (3.39)	5.84 (5.89)	6.93 (6.73)	43.66 (43.58)
$Et_2PbGbha$(b) (black)		42.67 (42.93)	4.07 (4.01)	5.55 (5.56)	6.55 (6.35)	40.99 (41.15)
$Ph_2PbGbha$(b) (black)		52.12 (52.07)	3.56 (3.36)	4.77 (4.67)	5.26 (5.34)	34.49 (34.56)

a) Symbols as under Discussion, this paper

b) No melting below 350°C

Table 2

IR-data

1) H_2Salen (in the 400–250 cm^{-1} range): 375 w; 360 w; 315 m; 280 vw. The spectrum in the 4000–400 cm^{-1} region essentially corresponds to that in KBr disks[34]).
2) H_2Gbha: 3380* vs; 3100–2800*, group of weak bands; 1600 s; 1500* vs; 1475* sh; 1455* sh; 1440* m; 1400* m; 1345 s; 1335 sh; 1310 s; 1290 w; 1270 m; 1260 vs; 1220 vs; 1150 vs; 1135 sh; 1110 s; 1035 s; 1020 ms; 975 s; 960 sh; 925 m; 910 vw; 895 w; 875 m; 855 m; 840 vs; 760 s; 750 vs; 740 s; 730 vs; 725 s; 615 s; 550 sh, bd; 520 m; 450 vs; 415 bd; 280 m.
3) $Me_2PbSalen$: 3200–2700*, group of weak bands; 1625 vs; 1595 s, sh; 1535 s, bd; 1470* s; 1440* vs, bd; 1390* s; 1340 s; 1330 s; 1305 s, bd; 1260 vw; 1245 m; 1185 s; 1165 ms; 1150 ms; 1125 s; 1095 w; 1045 vs; 1030 s; 980 w; 965 vw; 940 m; 930 sh; 900 vs; 860 w; 825 m, bd; 785 w; 760 ms; 755 ms; 730 vs; 640 ms; 630 sh; 595 vs; 575 m, bd; 565 m, bd; 540 sh, bd; 520 w; 455 s; 435 w; 385 w; 360 vs; 325 w; 270 w.
4) $Et_2PbSalen$: 3400–2600*, group of weak bands; 1620 vs; 1595 s, sh; 1535 s, bd; 1465* vs; 1445* vs; 1400* s; 1370* vw; 1340 vs; 1330 vs; 1320 s; 1260 vw; 1245 ms; 1205 vw; 1180 s; 1170 s; 1150 vs; 1130 s; 1095 w; 1050 ms; 1030 ms; 975 ms; 970 ms; 945 m; 935 sh; 905 vs; 860 vw; 845 vs; 780 m; 775 sh; 755 s; 735 s; 710 w; 640 m; 630 vw; 600 s; 580 m, bd, d; 565 w, bd; 545 sh, bd; 510 w; 455 s; 435 w; 380 sh; 360 vs; 335 sh; 320 sh; 260 m.
5) $Ph_2PbSalen$: 3100–2800*, group of weak bands; 1625 s; 1615 vs; 1570 w; 1525 s; 1470* m; 1460* s; 1445* vs; 1435* m; 1430* s; 1405* ms; 1390* ms; 1355* m; 1340 ms; 1330 w; 1320 m; 1240 m; 1180 m; 1140 s 1125 m; 1120 w; 1090 vw; 1080 vw; 1060 vw; 1045 m; 1020 m; 1015 w; 1000 w; 995 m; 980 w; 970 vw; 950 vw; 915 vw; 905 ms; 860 vw; 845 m; 780 w; 775 vw; 755 vs; 740 ms; 720 vs; 685 ms; 635 w; 630 vw; 610 vw; 595 s; 580 w; 560 w; 545 sh; 510 vw; 480 vw; 455 w; 450 vs; 430 vw; 380 w; 360 vs; 340 w; 270 vs.
6) $Me_2PbGbha$: 3100–2900*, group of weak bands; 1585 vs; 1555 w; 1535 m, bd; 1495* s; 1450* vs, bd; 1400* sh; 1370 m; 1345 ms; 1335 sh; 1320 ms; 1285 vw; 1270 vw; 1260 s; 1250 ms; 1240 sh; 1220 w; 1195 vw; 1160 ms; 1140 ms; 1115 vw; 1030 vw; 1010 vs; 940 w; 885 w; 870 vw; 840 w; 795 m; 760 m; 750 vs; 745 sh; 735 s; 720 sh; 605 vs; 580 m, bd; 565 m, bd; 540 m, bd; 480 m; 410 m; 340 m; 280* w.
7) $Et_2PbGbha$: 1585 s; 1550 w; 1535 m, bd; 1485* s; 1450* vs, bd; 1425* s; 1370* m; 1345 sh; 1335 sh; 1320 s; 1290 vw; 1260 s; 1250 ms; 1240 sh; 1220 m; 1195 vw; 1155 ms; 1140 s; 1120 vw; 1030 m; 1010 s; 940 m; 895 vw; 880 w; 875 vw; 840 ms; 795 ms; 760 sh; 750 s; 740 vs; 735 vs; 720 sh; 700 vw; 605 m; 580 w, bd; 560 m, bd; 535 w, bd; 480 m; 410 m; 340 m; 280* w.
8) $Ph_2PbGbha$: 3100–2900*, group of weak bands; 1600 sh; 1585 s; 1565 m; 1550 vw; 1535 s; 1490* s; 1475* s; 1450* s; 1435* s; 1375* s; 1335 s; 1320 vs; 1290 vw; 1270 vw; 1260 vs; 1240 m; 1220 w; 1195 vw; 1155 ms; 1140 s; 1120 m; 1030 m; 1010 vs; 995 s; 940 m; 880 m; 865 w; 840 m; 795 m; 755 sh; 745 vs; 740 sh; 730 vs; 685 m; 605 m; 580 w; 565 w; 540 w; 485 w; 455 m; 410 w; 335 w; 280 w; 260 w.

The infrared spectra were measured on nujol and hexachlorobutadiene (HEBT) mulls using a Perkin-Elmer Mod. 457 spectrometer, CsI disks, in the wavenumber region 4000—250 cm^{-1}. The results are reported in Table 2. Starred figures refer to HEBT mulls. Values are accurate within ± 3 cm^{-1} for the range 2000—250 cm^{-1}, and within ± 10 cm^{-1} for 4000—2000 cm^{-1}. S = strong; v = very; m = medium; w = weak; sh = shoulder; bd = broad.

The electronic spectra were determined on freshly prepared solutions with a Beckman DK-2A instrument, 10 mm cells, on anhydrous CH_3OH solutions, blank CH_3OH. Solutions of Na_2Salen and Na_2Gbha were obtained by addition to H_2Salen and H_2Gbha of 20:1 excess CH_3ONa. The results are reported in Table 3. The spectrum of Ph_2PbGbha could not be taken owing to insufficient solubility.

Conductance measurements were performed on freshly prepared solutions with a LKB conductolyzer at 25 °C on 5×10^{-3} M solutions of Alk_2PbSalen in dimethylsulfoxide. The two solutions were practically not conducting. Insufficient solubilities did not allow measurements on the other complexes listed in Table 1.

PMR spectra were recorded at 25 °C with JEOL C 60 and Varian A 60 spectrometers, operating at 60 MHz, on nearly saturated solutions, using TMS as internal standard. The results are reported in Table 4. Compounds Ph_2PbSalen and R_2PbGbha were not investigated owing to their insufficient solubilities.

Discussion

The occurrence of chelation in solid R_2PbSalen is suggested by the infrared spectra, when compared with the spectra of H_2Salen and its metal chelates, M^{II}Salen[24–26]) (see under Experimental, this paper). The relevant vibrational bands of H_2Salen, missing in R_2PbSalen, are at 3100—2800 cm^{-1} (ν(OH) hydrogen bonded to the azomethine nitrogen[24])), 1285 cm^{-1} (hydrogen bonded OH in-plane bending[24])) and 860 cm^{-1} (hydrogen bonded out-of-plane bending[24])). Chelation is also indicated by shifts of ν(C=N) and ν(C—O) occuring in R_2PbSalen with respect to H_2Salen.

The first vibrational mode, ν(C=N), may be associated to the weak band at 1530 cm^{-1} of H_2Salen[24]), and to the strong bands at 1535 cm^{-1} of Alk_2PbSalen (1525 cm^{-1} for Ph_2Pb-Salen); or, alternatively, to the H_2Salen strong absorption at 1635 cm^{-1}, shifted to 1625—1620 cm^{-1} in R_2Pb Salen, according to assignments for Cu^{II} and Ni^{II}Salen complexes[25])[26]). The second, ν(C—O), could occur for H_2Salen at 1105 cm^{-1}, sh, as well as at 1320 cm^{-1}, w, and for R_2PbSalen at 1095—1090 cm^{-1} or at 1320—1305 cm^{-1}, following different assignments for Ni^{II}Salen[24])[25]). Whatsoever the right assignments are, the R_2PbSalen bands in the double bond region (1625—1525 cm^{-1}) closely correspond to those of M^{II}Salen chelates[24–26]), and the same occurs for bands attributable to ν(C—O).

Skeletal vibrations associated to M^{IV}—O and M^{IV}—N bonds were assumed to occur at 600 and 400 cm^{-1} in R_2SnSalen[22]), and may be related in some way with the strong bands at 600—595 cm^{-1} and 360 cm^{-1}, respectively, of R_2Pb Salen (both bands are missing in H_2Salen).

---

[24]) K. Ueno and A. E. Martell, J. physic. Chem. **60**, 1270 (1956).

[25]) E. J. Olzewski and D. F. Martin, J. inorg. nuclear Chem., **26**, 1577 (1964).

[26]) L. V. Interrante and J. C. Bailar, Inorg. Chem. [Washington] **3**, 1339 (1964).

On the other hand, the latter assignments are very tentative, ν(PbO) being attributed, inter alia, to bands at 391 cm^{-1} for Me_2Pb (acetylacetonate)$_2$^{6}), at 425 cm^{-1} for the aquo-ions Me_2Pb^{IV}^{7}), at 508 and 431 cm^{-1} for $Pb(OCH_3)_2$^{27}), and there existing no band assignments, to our knowledge, concerning $Pb^{IV}—N$ bonds.

It may be concluded that R_2PbSalen are chelated complexes, where the Pb^{IV} atom is six-coordinated by ONNO ligand atoms and C, C atoms of the organic residues.

Carbon-lead skeletal vibrations in Me_2Pb^{IV} derivatives, which in principle can indicate the configuration of the CPbC moiety, are expected around 541—523 cm^{-1}, $\nu_{as}(PbC_2)$^{2})^{6}), and 460—447 cm^{-1}, $\nu_s(PbC_2)$^{2}).

In Alk_2Pb Salen, the first could occur in the range 580—540 cm^{-1}, where is observed an increase of intensity and a broadening of the group of three bands there occurring, with respect to the corresponding bands of Ph_2PbSalen. Eventual symmetrical modes are obscured by ligand vibrations. In fact, the bands occurring at 455 and 435 cm^{-1} in Alk_2PbSalen correspond to analogous bands of Me_2SnSalen^{22}).

The infrared spectra of solid R_2PbGbha are mutually very similar (apart from R_2Pb^{IV} vibrations^{2})^{3})), essentially corresponding to the spectrum of Na_2Gbha^{19}) in KBr disks for the range 1500—700 cm^{-1}.

The 3400 cm^{-1} band, ν(NH), of H_2Gbha^{19})^{20}) disappears in R_2PbGbha (Experimental, this paper), and ν(C=N) (assumed to occur at 1613 cm^{-1} in H_2Gbha^{20}) and 1640 cm^{-1} in Na_2Gbha^{19})) is shifted to 1535 cm^{-1} in R_2PbGbha. This indicates the presence of $Gbha^{2-}$ in the Schiff base form and the coordination of the azomethinic nitrogen to lead. The strong or medium bands at 605 cm^{-1} could be tentatively associated to $Pb^{IV}—O$ bonds, and those around 335—340 cm^{-1} to $Pb^{IV}—N$ bonds. $\nu_{as}(PbC_2)$ could occur around 580—535 cm^{-1}, where the group of three bands is much more intense and broad for Alk_2PbGbha than for Ph_2PbGbha. It is worth to note that no coordinated ligand vibrations take place around 460 cm^{-1} (the Ph_2Pb Gbha band at 455 cm^{-1} being probably the $Pb—C_6H_5$ y-mode in Whiffen's notation^{3})); then, the absence of any absorption around 460 cm^{-1} for Alk_2Pb Gbha would imply that $\nu_s(PbC_2)$ is infrared inactive, i. e., the CPbC skeleton is linear^{2})^{4})^{6}).

It may be concluded that R_2PbGbha, at the solid state, contain $Gbha^{2-}$ (Schiff base form) coordinating R_2Pb^{IV} through the ONNO atoms, and that, at least for Me_2PbGbha, the CPbC moiety assumes a linear configuration.

The configuration of R_2PbL in solution phase is discussed in the following on the basis of electronic and PMR spectra, and of conductance measurements.

The two bands of H_2Salen, occurring at low energies^{28}) (maxima at 317 nm and 405 nm in CH_3OH solution), were attributed to a transition involving the whole molecule in the form of the predominating OH tautomer, with intramolecular H bonds to the azomethinic nitrogen (i.e. a, 300 nm stilbene type band)^{28}), and to an allowed transition of the NH tautomer (the "long wavelength band"^{28}); in CH_3OH, $C = 5.14 \times 10^{-4}$ M,

---

[27]) E. Amberger and R. Hönigschmid-Grossich, Chem. Ber., **98**, 3795 (1965).

[28]) M. D. Cohen and S. Flavian, J. chem. Soc. [London], Sect. B, **1967**, 321; and Ref. therein.

D = 0.72 at 405 nm). The predominant presence in solution phase of the OH tautomer is also inferred from the PMR spectrum (Table 3), where single signals occur for the ethylene bridge protons, while doublets would be expected for the NH tautomer[29].

The electronic spectra of Na_2Salen and R_2PbSalen (Table 3) consistently differ from that of H_2Salen, the OH and NH tautomer bands disappearing. The similarity of Na_2Salen and R_2PbSalen spectra suggests analogous ligand configurations, presumably in the dianion SCHIFF base form. The occurrence of bands at lower energies would imply chelation on the metal center[21]. Dissociation is excluded by the non-conducting character of R_2PbSalen solutions (see Experimental).

Table 3

Electronic Absorption Spectra in Methanol. The wavenlengths (λ, nm) and Absorptivities (ε, M^{-1} cm^2) refer to Band Maxima and Shoulders (sh)

Compound[a]	λ	log ε	λ	log ε	λ	log ε	λ	log ε	λ	log ε
Na_2Salen	230	4.73	261	4.26	270 (sh)	4.20	347	4.17		
Me_2PbSalen	241	4.70	260 (sh)	4.23	270 (sh)	4.11	362	3.83		
Et_2Pb Salen	(b)		260 (sh)	4.21	270 (sh)	4.11	346	3.98		
Ph_2Pb Salen	240	4.83			271 (sh)	4.27	376	3.95		
Na_2Gbha	235	4.19	292	3.85	348	3.60	450 (sh)	3.64	515	3.73
Me_2PbGbha	225	4.42	~275 (sh)	3.70	378	3.90	~500 (sh)	3.81	610	4.23
Et_2PbGbha	~235 (sh)	4.10	~275 (sh)	3.40	380	3.55	~510 (sh)	3.42	620	3.88

a) Symbols as under Discussion, this paper   b) No maximum detected for $\lambda \geqq 220$ nm

Table 4

PMR spectra of H_2Salen, Me_2PbCl_2 and Me_2PbSalen. T = 25 °C, $\delta_{TMS} = 0$

Compound	Solvent	(Pb)CH_3 δ(ppm)	$-CH_2-$ δ(ppm)	arom. δ(ppm)	$=CH-$ δ(ppm)	J(^{207}PbCH) (Hz)
H_2Salen[a]	$(CD_3)_2CO$		3.97	6.70–7.50	8.55	
Me_2PbCl_2	$(CD_3)_2SO$	2.25				155
Me_2PbSalen[b]	$(CD_3)_2SO$	1.76	3.77	6.20–7.40	7.94	177

a) Phenolic (O)H at 13.20 δ b) Unassigned signal of low intensity at 3.12 δ

The spectra of Alk_2PbGbha fully differ from that of H_2Gbha[18–20], showing that the benzoxazoline rings do not longer exist in the coordinated ligand. They differ also from the spectrum of Na_2Gbha (Table 3: our Na_2 · Gbha spectrum differs from literature reports[19][20], which probably concern mixtures of $Gbha^{2-}$ and H_2Gbha) for marked shifts to lower energies of the couple of bands at longer wavelengths, which could be due to an increase in per cent covalent character for the Pb-ligand bonds.

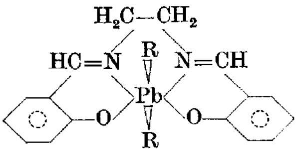
The structure of Me_2PbSalen in $(CD_3)_2SO$ solution (where the undissociated complex exists, according to the absence of conducting species) is clearly indicated by its PMR spectrum. Coordination of $Salen^{2-}$ on Pb^{IV} is suggested by the shift upfied of δ(Pb)CH_3 from Me_2PbCl_2 to Me_2PbSalen

---

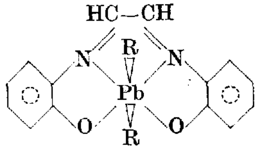
[29] G. O. DUDEK and R. H. HOLM, J. Amer. chem. Soc., **83**, 2099 (1961).

(Table 4). Similar effects, although less pronounced, were observed upon chelation by bis-bidentate ligands8) 33). The occurrence of sharp singlets for the (Pb)CH_3, —CH_2— (ethylene bridge) and =CH— signals strongly suggests that the magnetic environment is equivalent for all the above mentioned type of protons, from which the configuration (I) is inferred. A non-planar structure of Salen^{2-}, such as that occurring in Co^{III} acetylacetonate Salen etc.30), with bent CPbC, is expected to originate complex structures for any type of signal (due to magnetic anisotropy), such as those observed for RCo^{III}Salen31)32). Besides, the value of J(^{207}PbCH) is 177 Hz (the highest reported for Me_2Pb^{IV} derivatives), which is fully consistent with a linear CPbC skeleton4)7)8)33).

In conclusion, we propose the octahedral type configurations(I) and (II) as the more probable for the complexes R_2PbL, at the solid state and in solution. The ONNO ligand atoms would lie in a square plane, chelating linear R_2Pb^{IV} moieties.



I-R_2Pb Salen



II-R_2PbGbha

Structure (I) contains Salen^{2-} in its usual chelating dianion configuration34–37). A polymeric bis-bidentate configuration in the solid state cannot be excluded, although we are inclined to consider it rather improbable.

Acknowledgements — The financial support by NATO (Grant N° 301) and CNR (Roma) is gratefully acknowledged.

Palermo, Istituto di Chimica Generale ed Inorganica, University of Palermo.

Bei der Redaktion eingegangen am 16. April 1971.

Anschr. d. Verf.: Dr. Francesca Di Bianca, Dr. Eleonora Rivarola, Dr. G. C. Stocco und Prof. Dr. R. Barbieri, University of Palermo, Istituto di Chimica Generale, 26—28, Via Archirafi, 90123 Palermo (Italia)

---

30) M. Calligaris, G. Nardin and L. Randaccio, Chem. Commun. **1969**, 1248; **1970**, **1079**.

31) H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni and G. Costa, J. organometallic Chem. [Amsterdam] **11**, 167 (1968).

32) C. Floriani, M. Puppis and F. Calderazzo, J. organometallic Chem. [Amsterdam] **12**, 209 (1968).

33) R. Hönigschmid-Grossich and E. Amberger, Chem. Ber., **102**, 3589 (1969).

34) D. Hall and T. N. Waters, J. chem. Soc. [London] **1960**, 2644.

35) D. Hall and F. H. Moore, Proc. chem. Soc. [London], **1960**, 256.

36) E. N. Baker, D. Hall and T. N. Waters, J. chem. Soc. [London], Sect. A **1970**, 400; 406.

37) M. Calligaris, G. Nardin, L. Randaccio and A. Ripamonti, J. chem. Soc. [London] Sect. A **1970**, 1069.