Journal of Organometallic Chemistry, 81 (1974) 363—370
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INTERACTION OF DIMETHYLBIS(SUBSTITUTED OXINATO)LEAD WITH SOME DONOR MOLECULES IN SOLUTION

MITSUTOSHI ARITOMI and YOSHIKANE KAWASAKI

Department of Applied Chemistry, Osaka University, Suita, Osaka, 565 (Japan)

(Received June 4th, 1974)

Summary

The NMR and UV spectra of some dimethyl-lead(IV) and -tin(IV) complexes of alkyl-substituted oxines, $(CH_3)_2M(ox\text{-}Y)_2$ (M = Pb and Sn; ox-Y = methyl or ethyl substituted oxinato), were studied in several coordinating solvents. The $J(^{207}Pb—CH_3)$ values of these lead complexes except for 2-methyl- and 2-ethyl-oxinato complexes were found to increase with an increase in the solvent donor strength. We assumed that the changes of the $J(^{207}Pb—CH_3)$ values are due to the decrease of the excitation energy, ΔE, in the Fermi contact term produced by coordination of the solvent molecule to the lead atom. At the same time, the proton resonances of the methyl groups on the lead atom and also the 5-, 6- and 7-proton signals of the oxinato ligands shift to higher field. In contrast, the $J(^{119}Sn—CH_3)$ values of the tin complexes were found to be almost constant.

The stability constants of the above lead complexes with several organic phosphates have been measured spectrophotometrically in cyclohexane. A linear relationship was found between the stability constants and the basicities of these phosphates.

Introduction

Many organometallic oxinato complexes have been prepared, and their chelate structures and the metal—ligand interaction have been studied by X-ray crystallographic analysis or by the IR, NMR and UV spectra [1]. However, there have been few studies of the interaction between the complexes and donor molecules in solution. In dimethylbis(oxinato)tin, it has been shown that this complex has a stable hexacoordinate configuration even in strong donor solvents and the solvent molecules do no coordinate to the tin atom [2]. On the other hand, in hexacoordinate dimethyllead(IV) complexes, $(CH_3)_2PbX_2$ (X = acetylacetonato and benzoato), we found that the solvent coordinates to the lead atom [3, 4]. In the present paper, we report the preparation of some dimethyl-lead(IV) and -tin(IV) complexes of alkyl-substituted oxines, $(CH_3)_2M(ox\text{-}Y)_2$ (M = Pb and Sn; ox-Y = methyl- or ethyl-substituted oxinato), and studies of the interaction with several donor molecules in solution.

Experimental

Materials

Dimethyllead dichloride was prepared by the method reported previously [5 8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline were obtained from a commercial source. The other methyl- or ethyl-substituted 8-hydroxyquinolines were prepared by literature methods [6]. Organic phosphates and the solvents used in spectral measurements were reagent grade and purified according to standard methods.

The specific conductance of HMPA used in conductivity measurements was 9.80×10^{-7} ohm^{-1} cm^{-1}.

Preparation of dimethylbis(alkyl-substituted oxinato)-lead(IV) and -tin(IV), $(CH_3$, $M(ox\text{-}Y)_2$ (M = Pb and Sn; Y = H, 2-CH_3, 2-C_2H_5, 3-CH_3, 4-CH_3, 5-CH_3 and 7-CH_3

All lead complexes described here were prepared according to the following general procedure [7]. Dimethyllead dichloride (1.5 g, 5 mmol) was suspended in an aqueous solution (10 ml) of an appropriate methyl- or ethyl-substituted oxine (10 mmol). After adding aqueous ammonia (~ 5 ml) to this solution, the reaction mixture was stirred for 5 h and filtered. The yellow precipitates

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF $(CH_3)_2M(ox\text{-}Y)_2 \cdot L$

Compound			M.p (°C)	Analysis found (calcd.) (%)		
M	Y	L		C	H	N
Pb	2-CH_3		208 [b]	47.70 (47.73)	4.01 (4.01)	5.21 (5.06)
Pb	2-C_2H_5		235-237 [c]	49.51 (49.56)	4.06 (4.50)	4.75 (4.82)
Pb	3-CH_3	H_2O	153 [b]	46.01 (46.23)	4.25 (4.23)	4.75 (4.90)
Pb	4-CH_3	H_2O	181 [b]	46.50 (46.23)	4.01 (4.23)	4.99 (4.90)
Pb	5-CH_3	H_2O	110 [b]	45.99 (46.23)	4.48 (4.23)	4.69 (4.90)
Pb	7-CH_3	CH_3OH	104-106 [c]	47.06 (47.17)	4.39 (4.30)	5.23 (4.78)
Sn	2-CH_3		238 [b]	56.54 (56.81)	4.74 (4.77)	6.21 (6.02)
Sn	3-CH_3		244-246	56.68 (56.81)	4.80 (4.77)	5.94 (6.02)
Sn	4-CH_3		184-185	57.03 (56.81)	4.89 (4.77)	6.30 (6.02)
Sn	5-CH_3		229-231	56.61 (56.81)	4.80 (4.77)	6.15 (6.02)
Sn	7-CH_3		206-207	56.65 (56.81)	4.82. (4.77)	6.23 (6.02)

[a] Molar conductivity (ohm^{-1} cm^{2} mol^{-1}) at 3.0×10^{-3} (mol/l) in HMPA (25 ± 0.1°C). [b] Decomposes above these temperatures. [c] With small amounts of decomposition.

TABLE 2

ABSORPTION MAXIMA OF THE ^1L_a BAND AND THEIR log ε VALUES IN THE UV SPECTRA OF $(CH_3)_2M(ox\text{-}Y)_2$ (M = Pb AND Sn) IN SEVERAL SOLVENTS [a]

	M = Pb		M = Sn
Solvent	Y = H	Y = 2-C_2H_5	Y = H
C_6H_{12} [b]	391 (3.58)	382 [c] (3.69)	380 [c] (3.69)
Py	397 (3.64)	376 (3.60)	379 (3.72)
TMP [d]	398 (3.65)	372 (3.62)	375 (3.65)
DMSO	398 (3.66)	372 (3.61)	375 (3.62)
HMPA	405 (3.67)	375 (3.66)	376 (3.62)

[a] In nm (1.0×10^{-4} mol/l). The value in parentheses is log ε of the absorption maximum. [b] Cyclohexane. [c] In benzene. [d] Trimethyl phosphate.

obtained were recrystallized from methanol. Except for the 2-methyl- and 2-ethyloxinato complexes, the crystalline lead complexes contain one solvent molecule (H_2O or CH_3OH). All tin complexes described here were prepared according to the literature [8].

Analytical data and physical properties for newly prepared complexes of lead and tin are shown in Table 1.

Ultraviolet spectra

The ultraviolet spectra were recorded on a Hitachi model 356 spectrometer with

TABLE 3

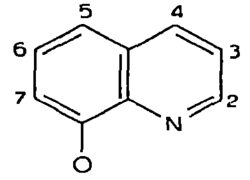
PROTON COUPLING CONSTANTS OF $(CH_3)_2M(ox\text{-}Y)_2$ (M = Pb AND Sn) IN SEVERAL SOLVENTS [a]

	M = Pb		M = Sn
Solvent	Y = H	Y = 2-C_2H_5	Y = H [b]
$CDCl_3$	152.5	137.3	71.2
CH_3OH	[c]	137.7	[c]
2-CH_3Py	166.5	136.2	71.1
4-CH_3Py	168.0	136.2	71.4
Py	167.3	136.8	71.5
TMP	173.4	[c]	70.2
DMF	175.6	138.0	69.6
DMSO	176.4	136.2	69.6
HMPA	187.2	138.3	69.0

[a] $J(^{207}Pb—CH_3)$ and $J(^{119}Sn—CH_3)$ values in Hz. [b] Values for 2-methyloxinato complex are 87.6 Hz in $CDCl_3$ and 88.2 Hz in pyridine. [c] Could not be observed because of poor solubility.

TABLE 4

PROTON CHEMICAL SHIFTS (δ) OF $(CH_3)_2M(ox\text{-}Y)_2$ (M = Pb AND Sn) IN SEVERAL SOLVENTS (in ppm) [a]



M	Y	Solvent	CH_3—M	2-H	3-H	4-H	5-H	6-H	7-H
Pb	H	$CDCl_3$	2.14	9.10	7.42	8.24	7.06	7.51	7.00
Pb	H	TMP	1.78	9.22	7.41	8.20	6.89	7.43	6.79
Pb	H	DMSO-d_6	1.70	9.22	7.51	8.25	6.76	7.28	6.65
Pb	H	HMPA	1.72	9.25	7.46	8.24	6.65	7.25	6.52
Pb	2-C_2H_5	$CDCl_3$	1.82		7.30	8.15	7.16	7.43	6.94
Pb	2-C_2H_5	DMSO-d_6	1.79		7.54	8.36	7.00	7.40	6.88
Pb	2-C_2H_5	HMPA	1.77		7.65	8.45	7.02	7.44	6.88
Sn	H	$CDCl_3$	0.44	8.57	7.19	8.12	7.30	7.59	7.08
Sn	H	TMP	0.28	8.50	7.38	8.40	7.16	7.61	7.16
Sn	H	DMSO	0.27	8.44	7.39	8.37	7.14	7.56	7.14
Sn	H	HMPA	0.23	8.48	7.35	8.39	7.24	7.56	7.11
Hox		HMPA		8.78	7.52	8.35	7.36	7.36	7.12
Naox [b]		HMPA		8.47	7.12	7.90	6.56	7.00	6.37
Hox·HCl		HMPA		9.26	8.12	9.19	7.66	7.75	7.66

[a] Chemical shifts of the ethyl group on the oxinato ligand are almost the same (δ(CH_3—CH_2): 1.45 ± 0.05 (triplet); δ(CH_3—CH_2): 3.03 ± 0.03 (quartet) ppm. The coupling constants, J_{23}, J_{24}, J_{34}, J_{56}, J_{57} and J_{67}, were found to be 4.2 ± 0.2, 1.5 ± 0.2, 8.0 ± 0.2, 8.1 ± 0.2, 1.1 ± 0.2 and 7.9 ± 0.2 Hz, respectively. [b] Sodium oxinate.

a 1 cm quartz cell. The absorption maxima and their log ϵ values of the oxinato co plexes of lead and tin in several solvents are shown in Table 2*.

Proton magnetic resonance spectra

The proton magnetic resonance measurements were made with a JEOL model JNM-PS-100 spectrometer (100 MHz at room temperature). The chemical shifts (δ were measured relative to tetramethylsilane as internal standard. The spectra for th 2-, 3- and 4-protons in the oxinato ligand were analyzed as the first order AMX system and those for the 5-, 6- and 7-protons as the ABC system by using the method reported previously [9] on a NEAC 2200 model 700 computer. The coupling constants and chemical shifts were slightly dependent on the concentration of the solute in the coordinating solvents (±1.0 Hz and ±0.02 ppm, respectively). The results for the coupling constants and chemical shifts obtained in about 2 wt% are summarized in Table 3 and 4, respectively.

---

* $(CH_3)_2Pb(ox\text{-}Y)_2$ (Y = 3-, 4-, 5- and 7-CH_3), $(CH_3)_2Pb(ox\text{-}2\text{-}CH_3)_2$ and $(CH_3)_2Sn(ox\text{-}Y)_2$ (Y = 2-, 3-, and 7-CH_3) compounds were found to behave in the same manner as $(CH_3)_2Pb(ox)_2$, $(CH_3)_2Pb(ox\text{-}2\text{-}C_2$ and $(CH_3)_2Sn(ox)_2$ compounds in the UV and PMR spectra, respectively. Thus, we discuss the latter thr compounds.

Determination of stability constants

The equilibrium 1 was assumed for the lead compound—donor molecule (R_3PO) systems in cyclohexane* as in $(CH_3)_2Pb(OCOC_6H_5)_2$—HMPA system [4]. The stability constant, K, was determined using eqn. 2 [10], where ϵ_0 and

$$(CH_3)_2Pb(ox\text{-}Y)_2 + R_3PO \overset{K}{\rightleftharpoons} (CH_3)_2Pb(ox\text{-}Y)_2 \cdot R_3PO \qquad (1)$$

$$\frac{1-(D_0/D)}{A_0} = -K + K(\epsilon_c/\epsilon_0)(D_0/D) \qquad (2)$$

ϵ_c are the molar extinction coefficients of the lead compound and its complexes, respectively. D_0 and D are the absorbances of a solution containing only the lead compound and a series of solutions containing a constant amount of the lead compound but varying amounts of R_3PO compounds. A_0 is the total concentration of R_3PO compounds.

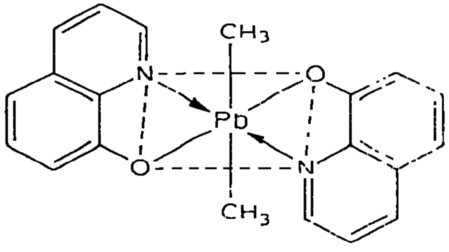
Results and discussion

Ultraviolet spectra

As shown in Table 2, the position of ^1L_a band in the UV spectra of $(CH_3)_2Pb(ox)_2$ shifts to longer wavelength and its ϵ value becomes larger by changing the solvent from cyclohexane to HMPA, while those of $(CH_3)_2Pb(ox\text{-}2\text{-}C_2H_5)_2$ and $(CH_3)_2Sn(ox)_2$ are almost the same. The above complexes were found to be non-electrolytes in HMPA (see Table 1). These results indicate that in strongly donor solvents both oxinato ligands coordinate to the lead atom as bidentate ligands [1]. The red shift of the absorption maximum with solvent shows that the coordination of nitrogen to lead is strengthened with increasing solvent donor strength, which is analogous to the results for metal—oxinato complexes [1].

Proton magnetic resonance spectra

The $J(^{207}Pb—CH_3)$ value of $(CH_3)_2Pb(ox)_2$ is comparable to the values of $(CH_3)_2Pb(acac)_2$ (154.7 Hz) [3] in $CDCl_3$, $(CH_3)_2PbCl_2$ (154.5 Hz) [11] and $(CH_3)_2Pb(ClO_4)_2$ (150.0 Hz) [11] in DMSO. The configuration for this compound, therefore, seems to be of the same type, the *trans*-configuration (I) [7, 12].



(I)

---

* From the fact that the ν(OH) stretching frequencies of the lead compounds, $(CH_3)_2Pb(ox\text{-}Y)_2 \cdot L$ (Y = 3-, 4- and 5-CH_3, $L = H_2O$: about 3680; Y = 7-CH_3, $L = CH_3OH$: 3640 cm^{-1}), in $CDCl_3$ are comparable to those of water and methanol in the same solvent (3680 and 3640 cm^{-1}, respectively), the water and methanol in the crystals are supposed to be completely free in cyclohexane.

The $J(^{207}Pb—CH_3)$ value of $(CH_3)_2Pb(ox\text{-}2\text{-}C_2H_5)_2$ in $CDCl_3$ is somewhat smaller than the above values and almost the same value as that of $(CH_3)_2Pb(OCOC_6H_5)_2$ in CH_2Cl_2 (136.8 Hz) [4] and that of $(CH_3)_2Pb(ClO_4)_2$ in water (135.1 Hz) [13].

The $J(^{207}Pb—CH_3)$ value of $(CH_3)_2Pb(ox)_2$ increases from about 152 to 187 Hz by changing the solvent from $CDCl_3$ to HMPA. The proton resonance of the methyl groups on the lead atom also shifts to higher field (see Table 4). The order of the solvents, which increase the J value of $(CH_3)_2Pb(ox)_2$ is the same as that of increasing donor number of the solvents [14]. Therefore, the above results are induced mainly by the coordination of the solvent molecule to the lead atom, as in $(CH_3)_2Pb(acac)_2$ and $(CH_3)_2Pb(OCOC_6H_5)_2$ [3, 4].

On the other hand, the $J(M—CH_3)$ ($M = {}^{207}Pb$ and ${}^{119}Sn$) values of $(CH_3)_2Pb(ox\text{-}2\text{-}C_2H_5)_2$ and $(CH_3)_2Sn(ox)_2$ are almost constant for all the solvents used in this experiment. The proton resonance of the methyl groups on the lead atom is almost constant. In this lead complex, the lead atom seems to be blocked by the 2-ethyl groups for coordination of the solvent molecule. This is not incompatible with the assumption that the seven-coordinate dimethyllead complex has a distorted pentagonal bipyramid configuration as in the case of the $(CH_3)_2Pb(OCOC_6H_5)_2\cdot$HMPA complex [4].

Generally the coupling mechanism for $J(M—CH_3)$ is considered to be governe by the Fermi contact term as expressed by the following equation [7]:

$$J(M—CH_3) = \text{const} \cdot \alpha_M^2 \cdot a_M(ns) \cdot a_H(1s)/\Delta E\ ,$$

where α_M^2 is the s character of the metal orbitals in the metal—carbon bonds, $a_M(ns)$ and $a_H(1s)$ is the hyperfine coupling constant of the ns electron in the metal atom and the 1s electron of a proton, respectively. ΔE is the mean singlet-triplet excitation energy. Thus, if only the change of α_M^2 is effective, the $J(^{207}Pb—CH_3)$ value for a dimethyllead compound with a linear C—Pb—C moiety is at most twice the value of $(CH_3)_4Pb$ (62.0 Hz) [15]. Therefore, the larger $J(^{207}Pb—CH_3)$ values as shown above may be due to either an increase in the hyperfine coupling constant, $a_{Pb}(6s)$, or a decrease in the excitation energy, ΔE. We consider that the decrease of the excitation energy due to an increase in the amount of negative charge around the lead atom plays a dominant role in the dimethyllead compounds in the coordinating solvents from the following experimental results: (1) the stability constants of dimethyllead complexes with donor molecules become larger with increasing donor strength (see Stability Constants), and (2) the proton resonances of the methyl groups attached to the lead atom shift to higher field *.

As shown in Table 4, in our oxinato complexes, the changes of the hetero ring proton chemical shifts with solvent are somewhat complicated while the phenolic ring proton chemical shifts in $(CH_3)_2Pb(ox\text{-}2\text{-}C_2H_5)_2$ and $(CH_3)_2Sn(ox)_2$ are almost constant. It is worthwhile to note that the 5-, 6- and 7-proton signals of $(CH_3)_2Pb(ox)_2$ shift to higher fields by about 0.40, 0.25 and 0.50 ppm by changing the solvent from $CDCl_3$ to HMPA and these signals in HMPA are close

---

* Previously we assumed that the amount of positive charge on the lead atom for $(CH_3)_2Pb(acac)_2$ becomes larger on the basis of the $J(^{13}C—H)$ values [3]. However, the $J(^{207}Pb—CH_3)$ values do not simply correlate with the $J(^{13}C—H)$ values. Details will be reported in the near future.

TABLE 5

VALUES OF THE STABILITY CONSTANTS OF $(CH_3)_2Pb(ox\text{-}Y)_2$ COMPLEXES WITH SOME DONORS IN CYCLOHEXANE

Donor	R	σ^* [b]	$\Delta\nu(OH)$ [c]	log K				
				Y = 7-CH_3	Y = 5-CH_3	Y = H	Y = 4-CH_3	Phenol [a]
				T 23±1°	T 20±1°	T 16±1°	T 24±1°	T 20°
R_3PO	$(CH_3)_2N$	0.65	450	2.32	2.16	2.40	2.29	3.18
R_3PO	s-C_4H_9O		350 [d]	1.80	1.82	1.79	1.77	
R_3PO	n-C_4H_9O		335 [d]	1.81	1.77	1.79	1.78	
R_3PO	C_2H_5O	1.35	345	1.80	1.76	1.78	1.78	2.61
R_3PO	CH_3O	1.46	315	1.75	1.70	1.77	1.78	2.26
R_3PO	p-$CH_3C_6H_4O$		245 [d]	1.30	1.31	1.50	1.51	
R_3PO	C_6H_5O	2.38	210	1.31	1.26	1.29	1.33	1.61
Py				0.33	0.32	0.33	0.34	
4-CH_3Py				0.32	0.34	0.35	0.32	

[a] Ref. 16. [b] Taft's σ^* value. [c] Frequency shift of the O—H stretching vibration of phenol: $\Delta\nu(OH) = \nu(OH)_{free} - \nu(OH)_{complex}$ (cm^{-1}). [d] Obtained in this work.

to those of sodium oxinate. The above change seems to indicate that the amount of negative charge on the phenolic ring is increased, as in $(CH_3)_2Pb(acac)_2$ [3].

Stability constants

The stability constants of $(CH_3)_2Pb(ox\text{-}Y)_2$ complexes with several organic phosphates (R_3PO), HMPA and pyridines in cyclohexane and for comparison, those of the hydrogen bonding complexes with phenol in CCl_4 [16] are shown in Table 5. The effects of the methyl substituent on the oxinato ligand on the stability constants are very small. As shown in Fig. 1, we have a linear relationship between the stability constants and the frequency shifts, $\Delta\nu$, of the O—H band of phenol when it is participating in hydrogen bonding with the R_3PO compounds. The stability constants increase with an increase in the electron density on the phosphoryl oxygen in the R_3PO compounds.

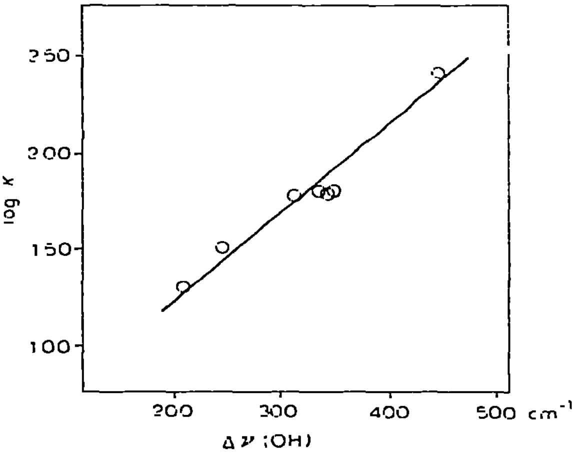


Fig. 1. Stability constants of R_3PO complexes with dimethylbis(oxinato)lead vs. the frequency shifts.

Conclusion

It was found that $(CH_3)_2Pb(ox\text{-}Y)_2$ interact with the coordinating solvents but the corresponding tin complexes do not.

From the measurements of the PMR and UV spectra of the lead complexes in the coordinating solvents and the stability constants with several organic phosphates and HMPA in cyclohexane, we have found that the interaction between the lead atom and the donor molecule becomes larger and the amount of negative charge around the lead atom is increased with increasing donor strengt The increase of the $J(^{207}Pb\text{—}CH_3)$ values and the high field shifts of the methyl proton signals on the lead atom are explained by the accumulation of negative charge around the lead atom.

Acknowledgements

We wish to express our hearty thanks to Professor Rokuro Okawara for his continuous encouragement throughout this study. We are also grateful to Drs. Masanori Wada, Yoshio Matsumura and Hideo Kurosawa of Osaka University for their helpful discussions.

References

1 Y. Kawasaki, Org. Magn. Resonance, 2 (1970) 165, and ref. therein.
2 W. Kitching, J. Organometal. Chem., 6 (1966) 249.
3 M. Aritomi, Y. Kawasaki and R. Okawara, Inorg. Nucl. Chem. Lett., 8 (1972) 69.
4 M. Aritomi, Y. Kawasaki and R. Okawara, Inorg. Nucl. Chem. Lett., 8 (1972) 1053.
5 G. Grütter and E. Kraus, Ber., 49 (1916) 1415.
6 J.P. Phillips, R.L. Elbinger and L.D. Merritt, Jr., J. Amer. Chem. Soc., 71 (1949) 3986; E. Noelting and E. Trautman, Ber., 23 (1890) 3666.
7 Y. Kawasaki, J. Organometal. Chem., 9 (1967) 549.
8 T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, J. Organometal. Chem., 1 (1964) 484.
9 C.A. Reilly and J.D. Swallen, J. Chem. Phys., 32 (1960) 1378.
10 M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, J. Organometal. Chem., 4 (1965) 308.
11 G.D. Shier and R.S. Drago, J. Organometal Chem., 6 (1966) 359.
12 Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 37 (1964) 903.
13 C.E. Freidline and R.S. Tobias, Inorg. Chem., 5 (1966) 354.
14 V. Gutmann, Coordination Chemistry in Nonaqueous Solutions, Springer, New York, 1968.
15 H.P. Fritz and K.E. Schwarzhans, J. Organometal. Chem., 1 (1964) 297.
16 T. Gramstad, Spectrochim. Acta, 20 (1964) 729.