

**SODIUM TETRALACTAMATOALUMINATES(1-).
A STUDY OF VALENCE VIBRATIONS OF LACTAM GROUPING
IN SODIUM 6-HEXANELACTAMATO-ISOBUTYLALUMINATES(1-)**

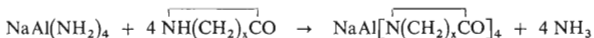
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Sodium tetralactamatoaluminate(1-) complexes have been prepared by reaction of sodium tetraamidoaluminate with 4-butanelactame, 6-hexanelactame, and 12-dodecanelactame, and their infrared spectra have been measured in the region from 600 to 4000 cm^{-1} . For assignment of some bands, a series of sodium 6-hexanelactamato-isobutylaluminates(1-) and 2-methoxyethoxy-lactamatoaluminates(1-) have been prepared. The bands in the region 1550–1650 cm^{-1} are discussed.

The sodium tetralactamatoaluminate complexes, $\text{NaAl}[\overline{\text{N}(\text{CH}_2)_x\text{CO}}]_4$ (*Ia, b, c*; $x = 3, 5, 11$, respectively), are well-soluble in ethers, aromatic hydrocarbons and partially soluble in aliphatic hydrocarbons. They can easily be prepared from sodium tetraamidoaluminate(1-) (ref.¹) by reaction with four equivalents of the corresponding lactam²:



In solution the compounds *I* are present as chemical individua. The analytically found ratio of aluminium to sodium to nitrogen is 1 : 1 : 4, and their infrared spectra are distinctly different from those of the starting lactams and from individual aluminium and sodium lactamates^{3,4}. By their solubility they differ from sodium salts of lower lactams which are practically insoluble both in aromatic and aliphatic hydrocarbons. Table I gives intensive and significant bands of the tetralactamatoaluminates *Ia–c* and, for comparison, also those of the individual lactams (*IIa–c*), sodium 6-hexanelactamate³ (*IIIb*), and aluminium 6-hexanelactamate (*IVb*).

The marked spectral bands of 6-hexanelactam (*Iib*), *i.e.* the valence vibration of hydrogen-bonded NH group at 3412 cm^{-1} and 3215 cm^{-1} and that of the whole amide group at 1675 cm^{-1} , either are not seen at all in the complex or simple lactamates, or they are very weak (being due to the polymer formed in the reaction or to the non-reacted lactam). Other marked spectral bands – at 2922 and 1436 cm^{-1}

TABLE I

Wave numbers of the marked bands in $\text{NaAl}[\text{N}(\text{CH}_2)_x\text{CO}]_4$ (I), lactams $\text{NH}(\text{CH}_2)_x\text{CO}$ (II), $\text{Na}[\text{N}(\text{CH}_2)_5\text{CO}]$ (IIIb), $\text{Al}[\text{N}(\text{CH}_2)_5\text{CO}]_3$ (IVb), and $\text{NaAl}[\text{N}(\text{CH}_2)_x\text{CO}]_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ (V) in 3% benzenic solutions. The compounds a,b,c, have $x = 3, 5, 11$, respectively

Compound	Wave numbers					
IIa	3 425 (w)	2 998 (s)	1 708 (vs)		1 460 (w)	1 390 (s)
	3 200 (s)	2 873 (w)			1 423 (m)	
Ia		2 990 (sS)	1 718 (s)	1 634 (s)	1 460 (m)	1 392 (s)
		2 955 (s)	1 705 (m)	1 600 (vs)	1 420 (w)	
		2 882 (w)				
VIIa		2 950 (m)	1 717 (w)	1 638 (s)	1 460 (w)	1 390 (m)
		2 918 (m)	1 700 (w)	1 600 (vs)	1 422 (m)	
		2 862 (s)				1 605 (m)
IIb	3 412 (m)	3 000 (s)				
	3 300 (sh)	2 922 (m)	1 675 (vs)		1 436 (m)	
	3 215 (m)	2 848 (w)				
Ib		3 000 (m)	1 675 (w)	1 630 (m)	1 444 (s)	1 390 (w)
		2 918 (vs)		1 611 (s)	1 427 (m)	
		2 845 (m)		1 587 (s)		
IIIb ^a			1 679 (w)		1 460 (vs)	1 379 (m)
		3 010 (vs)	1 674 (w)	1 612 (m)	1 529 (m)	
		2 924 (s)		1 598 (vs)		
IVb		2 856 (m)		1 582 (m)		
		3 032 (w)	1 676 (w)	1 604 (s)	1 485 (w)	
		2 995 (w)		1 583 (m)	1 462 (m)	
VIIb		2 907 (vs)		1 569 (vs)	1 446 (w)	
		2 835 (m)			1 424 (w)	
		3 430 (m)	3 000 (m)	1 681 (vs)	1 538 (w)	
IIc	3 338 (m)	2 920 (vs)			1 508 (s)	
		2 856 (m)			1 466 (vs)	
					1 445 (m)	
Ic		2 996 (w)		1 599 (s)	1 465 (w)	1 338 (w)
		2 918 (vs)		1 584 (m)	1 439 (s)	
		2 996 (w)		1 599 (s)	1 465 (w)	1 338 (w)
Ic		2 918 (vs)		1 584 (m)	1 439 (s)	
		2 848 (m)		1 554 (vs)	1 412 (m)	
				1 519 (m)		
VIIc		3 000 (w)	1 684 (w)	1 556 (s)	1 478 (w)	1 378 (m)
		2 918 (vs)	1 645 (m)	1 532 (m)	1 450 (m)	
		2 852 (m)			1 426 (w)	

^a According to ref.³ the spectrum was measured in solid phase in Nujol.

— are also present (with a certain shift) in 6-hexanelactamate ligand and in salts of lactam *IIa*. Four intensive bands at 1 566, 1 587, 1 611, and 1 630 cm^{-1} correspond to the NCO grouping (a shift by 45–115 cm^{-1} as compared with the free *Ib*). The insoluble *IIIb* rid of free lactam exhibits no bands in Nujol above 3 000 cm^{-1} , only a single very strong band at 1 460 cm^{-1} being assigned to amide group. A weak band at 1 679 cm^{-1} indicates the presence of *Ib* formed by hydrolysis³. Aluminium 6-hexanelactamate also exhibits no band above 3 100 cm^{-1} three bands being observed in the region of NCO stretching vibrations at 1 582, 1 598, and 1 612 cm^{-1} (ref.⁴). The other lactams and their salts and complexes exhibit similar behaviour to that of *Ib*.

Sodium tetralactamatoaluminates(1–) in benzene solution are predominantly in dimer form similar to *IVb* (ref.⁴). As already mentioned the region of NCO stretching vibrations of *Ib* contains four bands of approximately the same intensity within the range of 70 cm^{-1} , whereas in *IVb* a single band with two shoulders dominate within the range of 30 cm^{-1} . Due to the presence of sodium atom, the expected character of dimer formation of salts *I* will be different from that of *IVb* (ref.⁴). For assignment of bands of stretching vibrations of the individual NCO bonds in lactamate grouping, a series of compounds $\text{NaAl}[\overline{\text{N}(\text{CH}_2)_5\text{CO}}]_n(\text{iso-C}_4\text{H}_9)_{4-n}$ (*V*) have been prepared either by substitution reaction of 6-hexanelactam with sodium tetraisobutylaluminate(1–), $\text{NaAl}(\text{iso-C}_4\text{H}_9)_4$ (*VI*), or by reaction between *I* and *VI*. Moreover, a series of dilactamato-bis(2-methoxyethoxy)aluminates $\text{NaAl}[\overline{\text{N}(\text{CH}_2)_x\text{CO}}]_2 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ (*VIIIa–c*) have been prepared by reaction of the corresponding lactam with sodium dihydrido-bis(2-methoxyethoxy)aluminate(1–). In compounds *V* the bridges between two aluminium atoms or between an aluminium and a sodium atoms can only be formed by the lactam^{5–9}, whereas in compounds *VII* two types of ligands can contribute to solvation of sodium and aluminium.

The 1 450–1 750 cm^{-1} region of spectra of compounds *I*, *V*, and *VII* was submitted to band separation using a Hewlett–Packard 9825A computer, and wave numbers of the individual bands were determined along with their integrated intensities. Figure 1 shows, for example, both the whole spectrum of the given region and the individual separated bands for compounds *V* (n : 0.76; 3; 4). The corresponding bands with similar parameters were also obtained by separation of spectra of the other compounds *V* for $n = 0.3$ to $n = 4$. Dependence of wave numbers ν_{NCO} of the individual bands on number n in compounds *V* is given in Fig. 2. From this figure it is seen that wave number of the individual bands is constant up to $n = 1.5$, and above this value it is slightly increasing with n for three bands. Two bands about 1 603 and 1 620 cm^{-1} , which are quite distinct for $n = 2$ to $n = 3$, cannot be easily separated in other cases and coalesce into one broad band. A shift towards higher wave number in the case of two remaining bands ($\sim 1 550$ and $1 575 \text{ cm}^{-1}$) can be explained for the bands assigned to the solvating 6-hexanelactamate ligand where increasing n is

connected with decreasing number of acceptors, *i.e.* sodium atoms per one 6-hexanelactam unit¹⁰.

Fig. 3 shows dependence of relative integrated intensities (B) of the individual bands on n . The values of relative integrated intensities also depend on the separation procedure and can only serve for illustration of general trend of the individual bands. For small n values the dominant spectra band is at about 1550 cm^{-1} and is gradually replaced by another intensive band at about 1575 cm^{-1} . To lesser extent two other bands (three bands in the region from $n = 2$ to $n = 3$) are present whose intensity increases with increasing n . Literature gives several opinions about assignment of spectral bands of analogous compounds in the given region to individual vibrations. So *e.g.* for organometallic derivatives and salts of alkali metals and lactams, the individual bands are assigned to $\nu_{\text{C-O}}$ and $\nu_{\text{C-N}}$ vibrations^{11,12} or to vibrations of the whole NCO grouping in various structural and tautomeric arrangement⁸. Since with compounds V relative proportion of the individual bands changes with changing n , a single band being dominant in spectrum for $n < 1$, we presume all bands to belong to vibrations of NCO grouping in different structural environment.

Sodium ion of sodium tetraalkylaluminates(1-) forms strong complexes with compounds containing a donor oxygen atom^{13,14}. It can be presumed that in tight ion-pairs of sodium tetraisobutylaluminate(1-) ($V, n = 0$) the replacement of alkyl by lactamate ligand will result in such solvation of sodium cation with donor

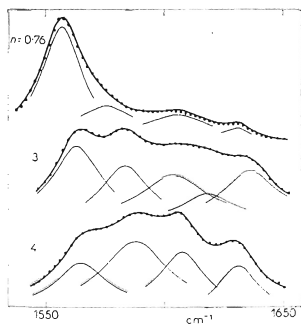


FIG. 1

The separated bands in ν_{NCO} vibration region of infrared spectrum of $\text{NaAl}(\text{i-C}_4\text{H}_9)_{4-n} \cdot [\text{N}(\text{CH}_2)_5\text{CO}]_n$ (Vb). The data: ● experimental points, — the separated bands, — the sum curve

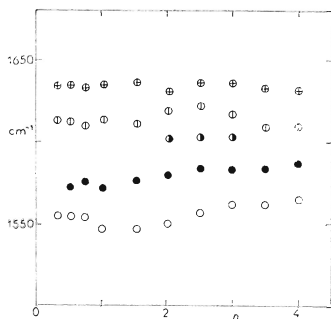


FIG. 2

The dependence on n of wave number of the individual bands in the region of ν_{NCO} vibrations of $\text{NaAl}(\text{i-C}_4\text{H}_9)_{4-n} \cdot [\text{N}(\text{CH}_2)_5\text{CO}]_n$ (Vb). The individual bands in the region $1550-1650\text{ cm}^{-1}$ are denoted in the order: ○ ● ⊙ ⊗

atom that the bond formed will be analogous to that in donor solvent (tetrahydrofuran, dimethylformamide, dimethyl sulphoxide, diethyl ether)... NaAlR_4 complex. Any further solvation of four-coordinated aluminium in the presence of non-solvated sodium is not likely^{15,17}. Therefore, we assign the band at about $1\,550\text{ cm}^{-1}$ to ν_{NCO} in $\text{Na}\dots\text{OCN}(\text{CH}_2)_5\text{-Al}$ grouping.

The second band at about $1\,575\text{ cm}^{-1}$ in spectrum of V increases rapidly with increasing n , having the same intensity as the band at $1\,550\text{ cm}^{-1}$ for $n\ 1\text{-}7$. From analogous solvation with oxygen ligand^{12,16,18} it can be expected that the NCO valence vibrations will be shifted to lower wave numbers with decreasing electron density at the metal atom, *i.e.* with decreasing number of the ligands solvating the metal. Furthermore, the absorption maximum of the solvating 6-hexanelactamate ligand can be expected to be shifted to higher wave numbers in the presence of the second $I\text{I}b$ molecule (*i.e.* a more electronegative ligand than isobutyl) at one aluminium atom^{19,20}. Obviously, the both factors condition formation of the band $1\,575\text{ cm}^{-1}$ during gradual substitution of isopropyl by lactam $I\text{I}b$ in V presuming the chain structure. If a sodium ion is solvated with two lactams $I\text{I}b$ in the middle of the chain, then at least one of $I\text{I}b$ is bound to aluminium atom by the second 6-hexanelactam ligand.

The third band at about $1\,611\text{ cm}^{-1}$ or $1\,603$ or $1\,620\text{ cm}^{-1}$, respectively, corresponds probably to the ligand forming the bridge between two aluminium atoms. For all the compounds V the given absorption is present to a lesser extent than the bands assigned to ν_{NCO} of the ligand solvating sodium cation, the respective relative intensity exceeding 25% in no case. It was found earlier²¹ for sodium alkoxohydridoaluminates and tetraalkoxoaluminates(1-) that coordination number of aluminium is 5 or even 6 in some cases. The five-coordinated aluminium is considered in struc-

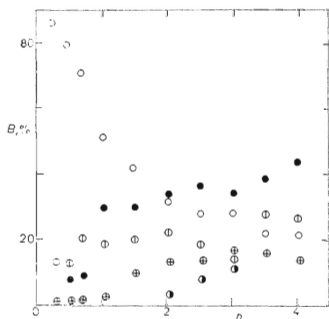


FIG. 3
Dependence of the relative integrated intensity (B) of the individual bands of the ν_{NCO} vibration region of Vb on n . For denotation of bands see Fig. 2

ture⁴ *IVb* whose infrared spectrum also contains a band at $1\,612\text{ cm}^{-1}$ besides the dominant band at $1\,598\text{ cm}^{-1}$. The assignment of the absorption at $1\,611\text{ cm}^{-1}$ to the ligand forming a bridge between two aluminium atoms is also supported by the fact that the bands at $1\,566$ and $1\,587\text{ cm}^{-1}$ are not observed in spectrum of *IVb*, and in solid *IIIb* a single NCO-group-sodium coordination makes itself felt by a band at a substantially lower wave number ($1\,460\text{ cm}^{-1}$). Relative intensity of the band $1\,611\text{ cm}^{-1}$ decreases in the compounds containing in their molecules also a small percentage of Al-NH-Al or Al-O-Al bridges (Table II), since the given bridges can obviously replace the bridges formed by lactamate ligand in structure of compound *I*.

The separation of individual bands of compound *VIIb* showed that the whole spectrum is shifted by $15\text{--}30\text{ cm}^{-1}$ to lower wave numbers in the ν_{NCO} region, the character of bands being maintained. The given shift can be explained, in accordance with the above-mentioned refs^{19,20}, by the presence of more electro-positive 2-methoxyethoxide ligand besides 6-hexanelactamate ligand at aluminium atom. This explanation of the shift of bands is also supported by the spectrum of sodium 6-hexanelactamato-2-methoxyethoxoaluminates(1-), $\text{NaAl}[\overline{\text{N}(\text{CH}_2)_5\text{CO}}]_n \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-n}$ (*Xb*, $n = 2.7\text{--}3.3$), in which the ν_{NCO} bands are found in the region between the bands of *Ib* and *VIIb* (Table III). If the ν_{NCO} absorption maxima in *Xb* correspond to the maxima in *Vb* shifted by as much as 15 cm^{-1} in some cases, then the dependence of relative intensities of bands on n of the compounds *XXb* (Fig. 4) is compatible with the presumption that the lactamate ligand is preferred to 2-methoxyethoxide in coordination at sodium atom. This stronger coordination of sodium cation to lactam or amide group as compared with that to 1,2-dimethoxyethane or tetrahydrofuran is known^{22,23}. The dominant band in spectrum of *Xb*

TABLE II

Wave numbers of NCO bands and the corresponding relative integrated intensities (*B*) in $\text{NaAl} \cdot (\text{NH})_{4-n}[\overline{\text{N}(\text{CH}_2)_5\text{CO}}]_n$ (*VIII*) and in $\text{NaAlCO}_{(4-n)/2}[\overline{\text{N}(\text{CH}_2)_5\text{CO}}]_n$ (*IX*)

Compound	ν_{NCO} (B)			
<i>VIII</i> , $n = 3, 5$	1 561 (25)	1 585 (40)	1 611 (20)	1 631 (15)
<i>VIII</i> , $n = 3, 9$	1 562 (22)	1 585 (41,4)	1 613 (19)	1 630 (14.5)
<i>VIII</i> , <i>IX</i> , $n = 4$	1 566 (20)	1 587 (42.5)	1 611 (25)	1 630 (12.5)
<i>IX</i> , $n = 3$	1 566 (27.5)	1 588 (43)	1 612 (15)	1 632 (14.5)
<i>IX</i> , $n = 3^a$	1 566 (22)	1 587 (39)	1 612 (22)	1 633 (17)

^a In the presence of 10 mol % of 6-hexanelactam (*IIB*).

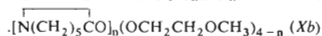
($n = 2$) is at $1\,562\text{ cm}^{-1}$, and that in spectrum of Vb ($n = 0.3-2$), where solvation of sodium atom with isobutyl group is highly unlikely, is at $1\,555\text{ cm}^{-1}$, i.e., also the band of the lowest wave number in the ν_{NCO} absorption.

In isopropoxy-6-hexanelactamatoalane, predominant role in formation of the bridge between two aluminium atoms of the dimer is played by oxygen atom of the alkoxy²⁴. Even in compounds Xb , intensity of the band of the bridge $I Ib$ ($1\,602\text{ cm}^{-1}$) is lower than that of lactamate Ib .

The fourth band at about $1\,632\text{ cm}^{-1}$, which has the highest wave number and the lowest relative intensity, belongs obviously to the terminal non-solvating 6-hexanelactame. In the spectrum of V it appears to a greater extent as late as at $n\,1.5$, and in none of the substances it exceeds 15%.

TABLE III

Wave numbers of NCO bands and the corresponding relative integrated intensities (B) in NaAl .



Compound	$\nu_{\text{NCO}} (B)$				
$Xb \equiv VIIb, n = 2$	1 554 (2)	1 562 (51)	1 583 (21)	1 601 (15)	1 613 (10)
$Xb, n = 2.67$		1 560 (31)	1 581 (32)	1 601 (26)	1 636 (11)
$Xb, n = 3$		1 562 (25)	1 581 (34)	1 604 (28)	1 630 (13)
$Xb, n = 3.33$		1 564 (22)	1 581 (37)	1 603 (28)	1 630 (13)
$Xb \equiv Ib, n = 4$		1 566 (20)	1 587 (42.5)	1 611 (25)	1 630 (12.6)

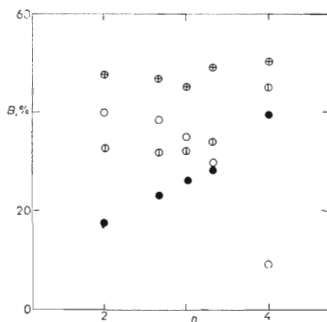


FIG. 4

Dependence of the relative integrated intensity (B) of the individual bands of the ν_{NCO} vibration regions of $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{4-n}[\text{N}(\text{CH}_2)_5\text{CO}]_n (Xb)$ on n . For denotation of bands see Fig. 2

EXPERIMENTAL

All the reactions and preparations of the studied compounds were carried out in a sealed apparatus under dry nitrogen. Sodium tetraamidoaluminate was prepared by direct synthesis¹, sodium tetralactamatoaluminates (*I*) were prepared by reaction of sodium tetraamidoaluminate with the corresponding lactam dissolved in benzene². The lactams were vacuum-distilled before use, the used solvents were dried by distillation from solutions of sodium dihydrido-bis(2-methoxyethoxy)aluminate. The relative molecular masses were determined cryoscopically in benzene within the concentration range 4–20%. The association degree was 1.8–2.0 for *Ia*, 2.1–2.05 for *Ib*, and 1.85–2.0 for *Ic*. The infrared spectra were measured with a Beckman IR 20A apparatus in 3–4% benzene solution.

The spectra were submitted to separation of bands using a Hewlett-Packard computer 9825A. The individual bands were approximated by the Lorentz curve, and the separation was carried out by the method of the greatest gradient.

Sodium diisobutyl-di(6-hexanelactamato)aluminate(1-) (*Vb*, $n = 2$) 3.02 g 20% solution of 6-hexanelactam (*Ib*) in benzene (5.34 mmol) was added drop by drop with stirring and cooling at room temperature to 2.05 g 36.3% solution of $\text{NaAl}(\text{i-C}_4\text{H}_9)_4$ (*VI*) in benzene (2.67 mmol). The reaction mixture was heated at 80°C 2 h and evaporated, the evaporation residue was dissolved in benzene to give a 3% solution which was used immediately for the measurements of spectra. The solution was analyzed, and the ratio Al : Na : N : i-C₄H₉ found was 1 : 1.02 : 2.03 : 1.96.

The other *Vb* with $n = 0.306$ to 3.5 were prepared in similar way. Also, *Vb* were prepared in parallel analogous procedure by reaction of *VI* with *Ib*. No substantial differences were found between spectra of the two *Vb* obtained in the two preparations.

Sodium Tri(6-hexanelactamato)-2-methoxyethoxyaluminate(1-) (*Xb*, $n = 3$)

4.87 g 20% solution of *Ib* in benzene (1.95 mmol) was added to 2.05 g (5.86 mmol) sodium tetrakis(2-methoxyethoxy)aluminate(1-) (ref.²⁵), and the solution obtained was heated to boiling 2 h. After cooling to room temperature the concentration was adjusted at 3%, and the solution was used for the spectral measurements.

The salts *X* with $n = 2$ were also prepared from the corresponding lactam *II* by addition of benzenic solution of the corresponding amount of sodium dihydrido-bis(2-methoxyethoxy)aluminate drop by drop with cooling at room temperature.

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REFERENCES

1. Časenský B., Macháček J., Kříž O.: Czech. 201 494.
2. Časenský B., Macháček J., Kříž O., Kubánek V.: Czech. 185 977.
3. Puffr R.: Private communication.
4. Kříž O., Časenský B.: This Journal 44, 2772 (1979).
5. Jennings J. R., Wade K., Wyatt B. K.: J. Chem. Soc., A, 1968, 2335.
6. Kay Y., Yasuoka N., Karai N., Kakudo M., Yasuda H., Tani H.: J. Organometal. Chem. 32, 165 (1971).
7. Mole T., Jeffery E. A.: *Organoaluminium Compounds*. Elsevier, Amsterdam 1972.
8. Yasuda H., Araki T., Tani H.: J. Organometal. Chem. 49, 103 (1973).
9. Tani H., Komoni T.: J. Polymer Sci., A-1, 4, 307 (1966).
10. Madan S. K.: *Coordination Chemistry*. Proc. John C. Bailar jr Sym. 1969, 139.

11. Stone M. E., Johnson K. E.: *Can. J. Chem.* *51*, 1260 (1973).
12. Tani H., Komoni T.: *J. Polymer Sci.*, A-1, *6*, 2295 (1968).
13. Bloor E. G., Kidd R. G.: *Can. J. Chem.* *46*, 3425 (1968).
14. Erlich R. H., Popov A. I.: *J. Amer. Chem. Soc.* *93*, 5620 (1971).
15. Schaschel E., Day M. C.: *J. Amer. Chem. Soc.* *90*, 503 (1968).
16. Day M. C., Olander J. A. *Amer. Chem. Soc.* *93*, 3584 (1981).
17. Starowieyski K. B., Pasynkiewicz S., Sporzynski A.: *J. Organometal. Chem.* *117*, 117 (1976).
18. Pasynkiewicz S., Starowieyski K. B., Peregudoc A. S., Kravtsov D. N.: *J. Organometal. Chem.* *132*, 191 (1977).
19. Duynstee E. F. J., H. van Raayen, Schmidt J., Veerkamp Th. A.: *Rec. Trav. Chim. Pays-Bas* *80*, 1313 (1961).
20. Irabayashi T. H., Itoh K., Sakai S., Ishii Y.: *J. Organometal. Chem.* *21*, 273 (1970).
21. Fusek J., Hanousek F.: *This Journal* *42*, 967 (1977).
22. Zaugg H. E.: *J. Amer. Chem. Soc.* *83*, 837 (1961).
23. Mayer U.: *Pure Appl. Chem.* *41*, 291 (1975).
24. Kříž O., Čásenský B., Macháček J.: *This Journal* *45*, 1366 (1980).
25. Čásenský B., Macháček J., Abrham K.: *This Journal* *36*, 2648 (1971).

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