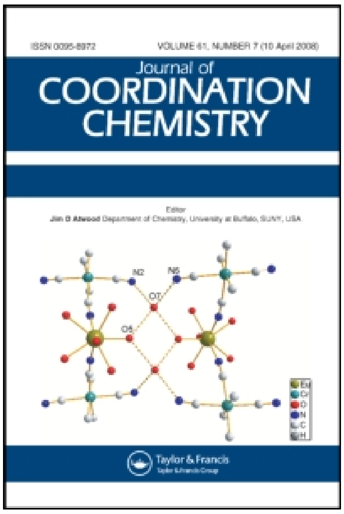

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# NEW COMPLEXES OF PALLADIUM(II) CHLORIDE WITH CHELATING PHOSPHORUS, SULFUR CONTAINING LIGANDS

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# NEW COMPLEXES OF PALLADIUM(II) CHLORIDE WITH CHELATING PHOSPHORUS, SULFUR CONTAINING LIGANDS

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New palladium(II) coordination compounds $PdLCl_2$ and $PdL_2Cl_2$ with chelating ligands containing thiophosphoryl groups along with carbamoyl or thiocarbamoyl groups were synthesized. The structures of the complexes in solutions and in solid were studied by electronic and IR spectroscopy, conductometry, and FD mass spectrometry. Transformations of the complex $PdL^3{}_2Cl_2$ under a strong electric field were investigated.

*Keywords:* palladium(II) chelate complexes; chelating ligands; phosphinosulfides

A number of $PdCl_2$ complexes with bidentate thiophosphoryl containing ligands — di(phosphinosulfides) have been described in the literature.[1,2] Investigation of composition and structure of such coordination compounds is of interest because the application of chelating ligands containing "soft" sulfur donor atoms for extraction of noble metals salts, and palladium(II) in particular, is promising.

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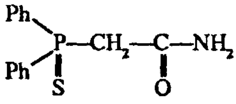
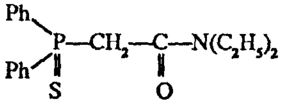
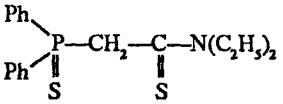
The present work deals with synthesis and properties of new palladium(II) complexes with chelating reagents containing a thiophosphoryl group with some other groups, capable of coordination to a metal ion. The structual formulas for the ligands used are given below:



$L^1$



$L^2$



$L^3$

Carbamoyldiphenylphosphinsulfidomethane ($L^1$) and N,N′-diethyl-carbamoyldiphenylphosphinsulfidomethane ($L^2$) was prepared as previously described.[3] The original synthesis procedure for N,N′-diethylthiocarbamoyldiphenylphosphinsulfidomethane ($L^3$) is given in the experimental section of the paper.

## EXPERIMENTAL

### Reagents

#### *N,N′-Diethylthiocarbamoyldiphenylphosphinsulphidomethane ($L^3$)*

Mixture of 2.5 g (7.5 mmol) of N,N′-diethylcarbamoyldiphenylphosphinsulphidomethane with 1.8 g (4.4 mmol) of the Lawesson reagent in 40 mL of $CH_3CN$ was boiled for 6 h Chloroform (70 mL) was added. Then the mixture was washed three times with ice water. The organic layer was separated, dried with $Na_2SO_4$, and the solvent was removed in *vacuo*. The solid remaining was recrystallized from a ether-hexane mixture. The product yield was 2.1 g (81%); m.p. 139–141 °C (acetone-hexane). *Anal.* Calcd. for $C_{18}H_{22}NPS_2$ (%): C 61.85; H 6.92; N 4.00; S 18.34. Found: C 61.74; H 6.37; N 3.56; S 18.29. $^{31}P$ NMR ($CH_2Cl_2$): $\sigma = 40.1$ (s). $^1H$ NMR ($CDCl_3$): $\sigma = 0.95$, 1.16 (6H, d t, $CH_3$, $^3J_{HH}$ 7.0.Hz), 3.67, 3.80 (4H, d q, $CH_2CH_3$, $^3J_{HH}$ 7.0 Hz), 4.3 (2H, d, $CH_2P$, $^2J_{PH}$ 14.4. Hz).

#### *$PdLCl_2$ ($L = L^1, L^2, L^3$)*

$PdCl_2$ (0.04 g; 0.2 mmol) was added to a solution of the phosphinosulfide ($L,^1$ $L^2$, $L^3$) (0.2 mmol) in chloroform (10 mL) and stored at room temperature. In 1–2 days the dark $PdCl_2$ dissolved completely, and in the cases of $L^1$ and $L^3$ small coloured crystals of the complexes $PdLCl_2$ appeared on the walls of the flask. Yields 70–80%. (Analytical data for the substances synthesized are given in Table 1). Complex $PdL^2Cl_2$ was obtained the same way but only in solution, because concentrating the latter was accompanied with precipitation of dark decomposition products.

### $PdL^3{}_2Cl_2$

0.07 g (0.2 mmol) of $L^3$ was added to a solution with an equimolar quantity (0.11 g) of $PdL^3Cl_2$ in 10 mL of chloroform. The solvent was removed in *vacuo*; the solid residue was washed with hexane and then filtered off. Yellow-orange $PdL^3{}_2Cl_2$ was recrystallized from chloroform. Yield 73%; m.p. 118 °C. Analytical data are given in the Table 1.

## Measurements

IR spectra for the complexes (KBr pellets) were recorded with "Specord 75-IR" ("Zeiss") spectrometer. A UV-VIS "Specord M-40" ("Zeiss") spectrometer was used for absorption spectra. Conductometry determinations were performed with a P5010 variable current bridge, the cell constant value being 0.20. The field desorption (FD) mass spectra were measured with a MI 1201 mass spectrometer. The details of the experiment can be found elsewhere.[4]

TABLE 1 Analytical data and some physical properties for the complexes synthesized

| Complex (brutto-formula, colour, m.p.) | Analytical data | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C, % | | H, % | | N, % | | Pd, % | |
| | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $PdL^1Cl_2$ ($C_{14}H_{14}PSONPdCl_2$, brown, 151 °C) | 37.15 | 36.94 | 3.12 | 3.05 | 3.09 | 3.15 | 23.51 | 22.94 |
| $PdL^3Cl_2$ ($C_{18}H_{22}PNS_2PdCl_2$, red-brown, 168 °C) | 41.20 | 40.99 | 4.23 | 4.18 | 2.67 | 2.59 | 20.28 | 20.19 |
| $PdL^3{}_2Cl_2$ ($C_{36}H_{44}P_2N_2S_4PdCl_2$, yellow-orange, 118 °C) | 49.57 | 49.31 | 5.08 | 5.14 | 3.12 | 2.96 | 12.20 | 12.00 |

## RESULTS AND DISCUSSION

Solid $PdCl_2$ dissolves completely in chloroform in the presence of an equimolar qunatity of the thiophosphoryl containing ligand ($L^1$, $L^2$ or $L^3$), giving in solution complex compounds of the general formula $PdLCl_2$ (see the EXPERIMENTAL section).

Chloroform solutions of the complexes $PdLCl_2$ were mixed with another equivalent of the corresponding ligand ($L^1$, $L^2$ or $L^3$). Unlike in the cases of $PdL^1Cl_2$ and $PdL^2Cl_2$, addition of $L^3$ led to noticeable changes in the absorption spectra of $PdL^3Cl_2$ (Figure 1). A new compound thus obtained, which was isolated from the reaction mixture as described in the EXPERIMENTAL section, has the formula $PdL^3{}_2Cl_2$.

Therefore, interaction of solid $PdCl_2$ with the phosphinosulfides ($L^1$, $L^2$, $L^3$) in chloroform can be described with the following equations:

$$PdCl_2(s) + L \rightleftarrows PdLCl_2 \rightleftarrows PdLCl_2(s) \qquad \textbf{(1)}$$

$$PdL^3Cl_2 + L^3 \overset{K}{\rightleftarrows} PdL^3{}_2Cl_2 \qquad \textbf{(2)}$$

Electronic spectra for the comlexes $PdLCl_2$ ($L = L^1, L^2$ or $L^3$) and $PdL^3{}_2Cl_2$ in chloroform are given in Figures 1 and 2. As all three phosphinosulfides absorb strongly in the region of 40000–30000 $cm^{-1}$, the UV spectra presented in Figure 2 are differential ones, obtained on chloroform solutions of the same corresponding concentrations as comparison solutions of the ligand.

The absorption spectrum for $PdL^3Cl_2$ is quite typical for square planar complexes of palladium(II) with the chromophore $[PdS_2Cl_2]$.[2,5] Charge transfer bands (CT) with $\nu_{max}$. 39200 $cm^{-1}$ and 31300 $cm^{-1}$ are caused by electron density transitions from chloride and sulfur atoms respectively to the metal ion (Figure 2). Palladium(II) *d-d* transfers develop as a shoulder in the region of 25000 $cm^{-1}$ (Figure 1). Coordination of another ligand $L^3$ molecule to Pd(II) does not lead to significant changes in the positions of the CT's Cl → Pd and S → Pd observed in the spectrum of $PdL^3Cl_2$, but it is accompanied by redistribution of the intensities of those bands. On the slope of the band 31300 $cm^{-1}$, instead of the *d-d* transition signal observed for $PdL^3Cl_2$, an intense shoulder appears in the region 27000–28000 $cm^{-1}$ (Figure 1). Changes in the absorption spectra testify to differences in the composition and structure of the complexes $PdL^3Cl_2$ and $PdL^3{}_2Cl_2$. The spectrum of $PdL^3{}_2Cl_2$ does not contain a band at 34000 $cm^{-1}$, which is characteristic for square planar Pd(II) complexes with a $[PdS_4]$ configuration.[6] Thus the palladium ions in this

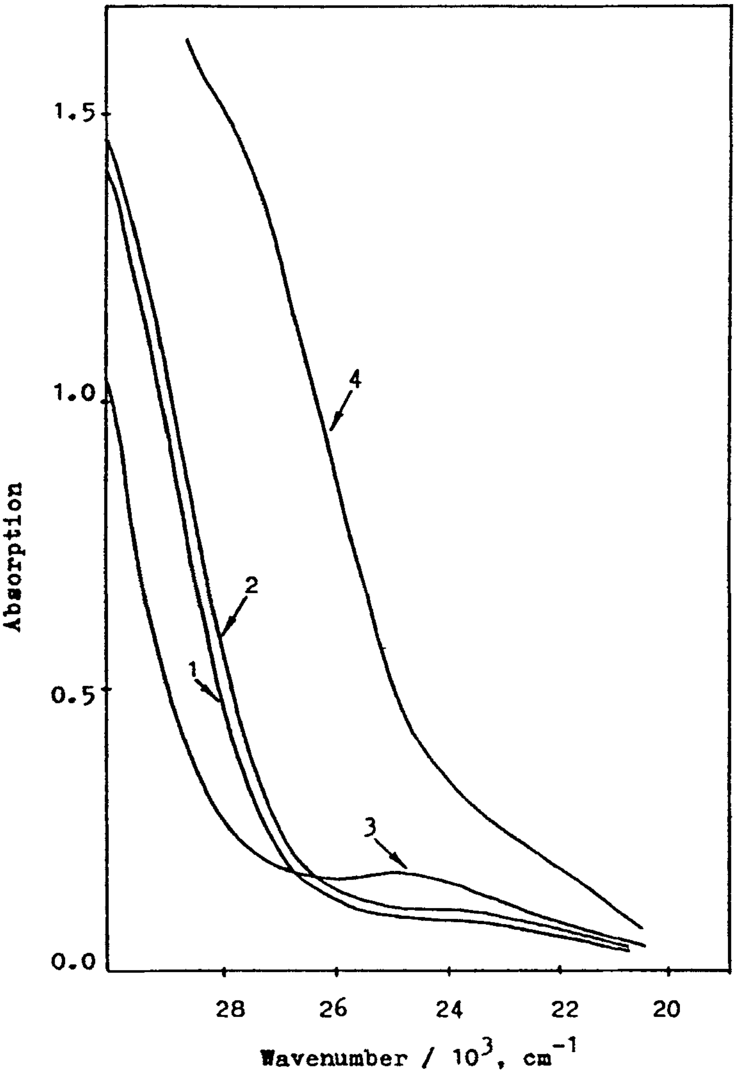


FIGURE 1 Absorption spectra of the complexes in chloroform solution ($C_{Pd}$ = $1.0 \cdot 10^{-3}$ M): 1 - $PdL^1Cl_2$; 2 - $PdL^2Cl_2$; 3 - $PdL^3Cl_2$; 4 - $PdL^3{}_2Cl_2$.

complex consist of both sulfur and chlorine atoms, but its geometry is different from square planar.

Electronic spectra for $PdL^1Cl_2$ and $PdL^2Cl_2$ are similar. This indicates the coordination geometry of the complexes is of the same type. There is an absorption band at 40000–38000 $cm^{-1}$ in the spectrum of $PdL^1Cl_2$ ($PdL^2Cl_2$), resulting from charge transfer (Cl → Pd) and also a CT (L →

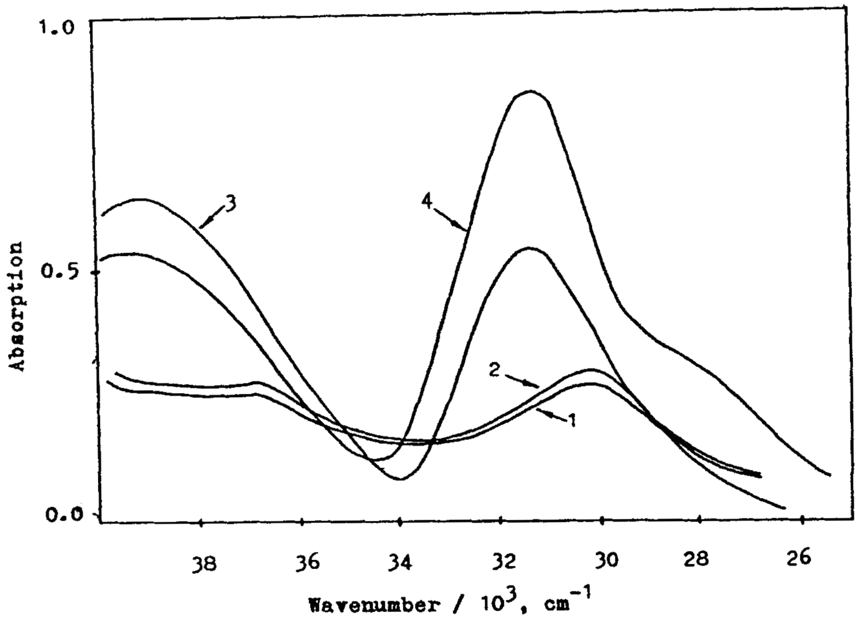


FIGURE 2 Differential absorption spectra of the complexes in chloroform solution ($C_{Pd} = 2.0 \cdot 10^{-4}$ M): 1– $PdL^1Cl_2$; 2 – $PdL^2Cl_2$; 3 – $PdL^3Cl_2$; 4 – $PdL^3_2Cl_2$. (Comparison solutions in chloroform: 1,2,3 – $C_L = 2.0 \cdot 10^{-4}$ M; 4 – $C_L = 4.0 \cdot 10^{-4}$ M).

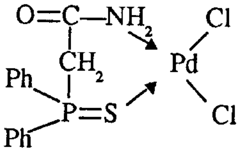
Pd) with $\nu_{max}$. 30300 $cm^{-1}$. *d-d* transitions for these complexes appear as a weak band at 24000 $cm^{-1}$.

Examination of IR spectra of the complexes $PdLCl_2$ ($L = L^1, L^3$) and $PdL^3_2Cl_2$ (Table 2) indicates that sulfur atoms of thiophosphoryl groups are involved in coordination with Pd(II). This is pointed to by bathochromic shifts, observed for the absorption bands in the region of valent oscillations for the P = S group.[7]

In the case of $PdL^1Cl_2$ the amide II band of the carbamoyl group is shifted by 25 $cm^{-1}$ towards longer wavelengths; amide I band shifts less (12 $cm^{-1}$). Significant bathochromic displacement is observed for the valent N-H oscillations. At the same time a very strong signal at 1440 $cm^{-1}$, attributed to valent oscillations of $CH_2$ group in the $-CH_2-\underset{\underset{O}{\|}}{C}-$ fragment, remains virtually unchanged in position. These data suggest the carbamoyl group of $L^1$ coordinates to Pd(II) by nitrogen. Therefore, the coordination arrangement of palladium in the square planar complex $PdL^1Cl_2$ is evidently $[PdSNCl_2]$.

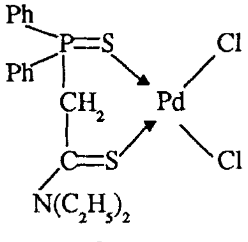
TABLE 2 Maximum wavenumber (cm$^{-1}$) for the bands in the IR spectra (KBr) of the ligands $L^1$, $L^3$ and their complexes with $PdCl_2$

| | $L^1$ | $PdL^1Cl_2$ | $L^3$ | $PdL^3Cl_2$ | $PdL^3{}_2Cl_2$ |
|---|---|---|---|---|---|
| $^{v}$PS | 621 | 618 | 635 | 620 | 620 |
| | 612 | 605 | 614 | 608 | 608 |
| | 586 | 575 | 587 | 577 | 577 |
| $^{v}$N–H | 3415 | 3390 | — | — | — |
| | 3310 | 3175 | | | |
| | 3155 | | | | |
| Amide I | 1690 | 1678 | — | — | — |
| Amide II | 1625 | 1600 | — | — | — |
| NCS I | — | — | 1514 | 1540 | 1535 |
| NCS II | — | — | 1403 | 1393 | 1395 |
| | | | 1353 | 1343 | 1350 |
| | | | 1342 | 1334 | 1338 |
| NCS III | — | — | 1103 | 1113 | 1103 |
| | | | | 1102 | |
| | | | 1080 | 1082 | 1077 |
| | | | | 1075 | |
| $^{v}$CS | — | — | 890 | 878 | 876 |



$PdL^1Cl_2$

In the $PdL^3Cl_2$ IR spectrum, besides bathochromic displacement of the bands attributed to valent P=S oscillations, essential changes in the positions and shapes for three groups of bands -N–C=S[8] are observed. These bands are complex, each containing contributions of valent C=S oscillations as well as oscillations C—N. NCS II bands undergo bathochromic shifting upon coordination of Pd(II) to $L^3$. Both strong NCS III oscillations are transformed into doublets, the components being close in intensity. Possibly, this is caused by oppositely directed displacement for the C—N and C=S increments of the NCS III band on complexation. On Pd(II) ion coordination to sulfur of the thiocarbamoyl the ν(C=S) stretch must undergo a low energy shift, and the ν(C—N) stretch a high energy one.[8] The NCS I band in the IR spectrum of $PdL^3Cl_2$, which bears the most important contribution of valent C—N oscillations, is shifted 26 cm$^{-1}$ to higher frequency, from the free ligand $L^3$ band. The strong stretch at 890 cm$^{-1}$ observed for $L^3$, which shows a 12 cm$^{-1}$ bathochromic shift on complexation, can be attributed to "pure"



$PdL^3Cl_2$

valent C═S oscillations. The facts above confirm the composition for the square planar complex $PdL^3Cl_2$ as $[PdS_2Cl_2]$.

The IR spectrum for $PdL^3{}_2Cl_2$ indicates the same band groups as for $PdL^3Cl_2$ (Table 2). Hence, coordination of $L^3$ molecules in the complex $PdL^3{}_2Cl_2$ is also by means of sulfur atoms of P═S and C═S groups.

Molar conductivity values for $1.0 \times 10^{-3}$ M solutions of $PdL^1Cl_2$ and $PdL^3Cl_2$ in acetonitrile are 4.51 and 8.78 $cm^2\ mol^{-1}\ Ohm^{-1}$, respectively. For a $PdL^3{}_2Cl_2$ solution of the same concentration the $\lambda$ value is 81.70 $cm^2\ mol^{-1}\ Ohm^{-1}$. It follows that the compounds $PdLCl_2$ are not electrolytes while $PdL^3{}_2Cl_2$ is 1:1 electrolyte.[10] This confirms the above conclusions, based on the electronic and IR data, that both chloride ions in the complexes $PdLCl_2$ are within the coordination sphere of Pd(II). In the case of $PdL^3{}_2Cl_2$ one of $Cl^-$ ions is coordinated with palladium ion, and another is counter-ion for the cation $[PdL^3{}_2Cl]^+$. Therefore, the Pd(II) coordination number in $PdL^3{}_2Cl_2$ is presumed to be five, the complex itself being distorted tetragonal pyramidal geometry.

From data obtained in the region 28500–24500 $cm^{-1}$ in the electronic spectra of $PdL^3Cl_2$ in chloroform solution after addition of $L^3$ till the concentrations ratio was 1:2, the formation constant K for the complex $PdL^3{}_2Cl_2$ (Eq (2)) was computed by using the PSEQUAD program.[11] The logK value thus obtained is $2.98 \pm 0.05$.

As $PdL^3{}_2Cl_2$ is a new type of Pd(II) complex with thiophosphoryl containing chelating ligands, detailed examination of this compound was of interest. In order to confirm the complex composition, and also to study its fragmentation under a strong electric field, $PdL^3{}_2Cl_2$ was investigated by means of field desorption (FD) mass spectrometry. The FD mass spectra show intense peaks of the pentacoordinated Pd(II) ions $[PdL^3{}_2Cl]^+$ (m/e = 837) and the ligand $L^3$ ions (m/e = 347), and also ions corresponding to $[PdL^3{}_2]^+$ (m/e = 804) and $[PdL^3Cl_2]^+$ (m/e = 524). At emitter temperatures above 290°C there are weak peaks with m/e>1400, which can be due to palladium cluster compounds. thus the peak at 1418 can be attributed to $[Pd_2L^3{}_3Cl_4 \cdot H_2O]$. (The emitter is known to contain a number of water molecules[12]). At the increased temperature 370–540°C intense peaks of $Pd^+$ ions are observed in the mass spectra. Note that the molecular ion peak for the complex $PdL^3{}_2Cl_2$ was not observes in the FD mass spectra.

The data obtained indicate the coordination compound exists in solution as $PdL^3{}_2Cl_2$ and in the solid state as a cluster which undergoes decomposition under a strong electric field. In this case the bond breaking in the multinuclear palladium(II) complex can proceed in two ways: with $[PdL^3{}_2Cl]^+$ particle formation or with disproportionation of palladium(II) into palladium(I) (ions $[PdL^3{}_2]^+$ and $Pd^+$) and palladium(III) (ions $[PdL^3Cl_2]^+$).

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## *References*

[1] E.W. Ainscough, H.A. Bergen, A.M. Brodie, K.A. Brown, *J. Chem. Soc.*, Dalton Trans., 1649 (1976).
[2] K.B. Yatsimirskii, G.G. Talanova, I.N. Kuraeva, M.I. Kabachnik, T.A. Mastryukova, I.M. Aladzheva, I.V. Leont'eva, *Dopov. Akad. Nauk* Ukraine, 147 (1994).
[3] I.M. Aladzheva, I.L. Odinets, P.V. Petrovskii, T.A. Mastryukova, M.I. Kabachnik, *Zh. Obshch. Khim.*, **63**, 611 (1993).
[4] V.G. Golovaty, R.N. Bondarenko, E.N. Korol, *Teor. Eksp. Khim.*, **11**, 349 (1975).
[5] D.A. Wheatland, C.H. Clapp, R.W. Waldron, *Inorg. Chem.*, **11**, 2340 (1972).
[6] C.K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes" (Pergamon Press, Oxford, London, New York, Paris, 1962), p. 287.
[7] R.R. Shagidullina, A.V. Chernova, V.S. Vinogradova, F.S. Mukhametov, The Album of IR Spectra of the Phosphorus Organic Compounds (the Interpreted Spectrogrammes) (Nauka, Moscow, 1984), p. 331.
[8] L.J. Bellamy, Advances in Infrared Group Frequencies (Mir, Moscow. 1971), p. 232.
[9] I. Susuki. *Bull. Chem. Soc. Japan*, **35**, 1286 (1962).
[10] W.J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).
[11] L. Zekany, I. Nagypal, Computational Methods for the Determination of Formation Constants (Plenum Press, New York, 1985), pp. 291–353.
[12] H.D. Beckey, Z. Naturforsch. A, 14, 712 (1959).