Synthesis, Structural and Multinuclear Natural Abundance $(^{13}\text{C},
^{31}\text{P},
^{195}\text{Pt})$ CP/MAS NMR Studies of Crystalline
$\text{O,}\text{O}^\prime\text{-Dialkylthiodiposphinate Platinum(II) Complexes}$

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Abstract—Platinum(II) O,O'-dicyclohexyl thiodiposphate [Pt(S$_2$P(O-cyclo-C$_6$H$_{11}$)$_2$)$_2$] (I) and platinum(II) O,O'-diisopropyl thiodiposphate [Pt(S$_2$P(O-isop-C$_3$)$_2$)$_2$] (II) complexes were obtained and studied by solid-state $^{13}$C, $^{31}$P, and $^{195}$Pt CP/MAS NMR spectroscopy. The thiodiposphate (Dtph) ligands in molecular structure I were found to be coordinated by platinum in S,S'-bidentate fashion to form the planar chromophore [PtS$_4$] (single-crystal X-ray diffraction data). For complex II, a new α-form (α-II) was obtained and identified by $^{31}$P MAS NMR spectroscopy. The $^{31}$P chemical shift anisotropy $\delta_{\text{aniso}}$ and the asymmetry parameter $\eta$ of the $^{31}$P chemical shift tensor were calculated from the whole MAS spectra.

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Most of the hitherto known platinum(II) O,O'-dialkylthiodiposphates are liquids or oily compounds [1]. Only two crystalline platinum complexes [Pt(S$_2$P(OR)$_2$)$_2$] have been structurally characterized: R = C$_3$H$_7$ [1] and iso-C$_3$H$_7$ [2]. In [3], we have demonstrated with single-crystal cooperite (natural PtS) as an example that $^{195}$Pt (both static and MAS) NMR spectroscopy can be employed for investigation of natural minerals of platinum. In cooperite, platinum(II) is included in square chromophores [PtS$_4$]. However, a structurally similar pattern has been found in dialkyl thiodiposphates [1, 2]: the metal atom is surrounded by four sulfur atoms making a slightly distorted square. That is why we found it interesting to obtain crystalline platinum(II) dialkylthiodiposphates and compare their $^{195}$Pt MAS NMR spectra and X-ray diffraction patterns.

In this study, we obtained the new complexes bis(O,O'-dicyclohexylthiodiposphate-S,S')platinum(II) (I) and bis(O,O'-diisopropylthiodiposphate-S,S')platinum(II) (II) of the general formula [Pt(S$_2$P(OR)$_2$)$_2$] (R = cyclo-C$_6$H$_{11}$ (I) and the α-form for R = iso-C$_3$H$_7$ (II)) and the magnetically diluted (with Pt(II)) isotope-substituted complex bis(O,O'-dicyclohexylthiodiposphate-S,S')platinum(II) [$^{63}$Cu(S$_2$P(O-cyclo-C$_6$H$_{11}$)$_2$)$_2$] (III). The structures of these complexes were studied by $^{13}$C, $^{31}$P, and $^{195}$Pt CP/MAS NMR spectroscopy and EPR spectroscopy; structure I was characterized by X-ray diffraction data.

EXPERIMENTAL

Synthesis. Crystalline complexes I and II were obtained by reactions of aqueous solutions of $K_2[PtCl_4]$ and appropriate salts K{S$_2$P(OR)$_2$}. The reaction mixtures were heated at 60°C for a short period of time and left overnight. The resulting yellow precipitates were filtered off, washed with water, and dried on the filter. Additional crops were obtained by extraction of the complexes from the mother liquors by chloroform. Single crystals of complex I for X-ray diffraction analysis were obtained from chloroform.

For EPR study, complex III was synthesized in the magnetically diluted state by mechanically grinding complex I with a small amount of CuCl$_2$·2H$_2$O (Cu : Pt = 1 : 1000). The use of this technique allows the molecules of complex III to be stabilized in the matrix of the platinum(II) complex. The content of the $^{63}$Cu isotope in CuCl$_2$·2H$_2$O was 99.3(1) at %.

1 Copper(II) O,O'-dialkyl thiodiposphates do not exist in the individual state because of prompt conversion into polynuclear copper(I) complexes [4] and the corresponding bis(O,O'-dialkylthiodiposphate-S,S') disulfides according to the intermolecular redox reaction:

\[ 4\text{Cu}^{2+} + 8(\text{RO})_2\text{P(S)}\text{S}^- = 4\text{Cu}([\text{S}_2\text{P(OR)}_2]_2] = [\text{Cu}_4([\text{S}_2\text{P(OR)}_2]_2] + 2(\text{RO})_2\text{P(S)}\text{S}^-\text{S}^-(\text{S})\text{P(OR)}_2]. \]
Crystalline complexes I and II and the starting potassium dithiophosphates were characterized by $^{13}$C MAS NMR spectroscopy:

Complex I, $\delta$: (1 : 2 : 1 : 2) 76.2, 76.1 (1 : 1, $-\text{OCH}_3$), 32.9, 32.2 (1 : 1, $\text{o-CH}_2$), 26.2, 26.0 ($\text{p-CH}_2$), 21.4, 20.8 ppm ($\text{m-CH}_2$).

$\text{K}[\text{S}_2\text{P(O-cyclo-C}_6\text{H}_11)_2]$, $\delta$: (1 : 2 : 3) 79.9, 78.8, 78.1, 77.1 (1 : 1 : 1 : 1, $-\text{OCH}_3$), 35.7, 35.2, 34.7, 33.9 ($\text{o-CH}_2$), 26.2 ppm ($\text{p-CH}_2$).

$\alpha$-II, $\delta$: (1 : 2) 74.1 ($-\text{OCH}_3$), 25.6, 26.2, 25.7, 25.0 ppm (1 : 1 : 1 : 1, $-\text{CH}_3$).

$\beta$-II, $\delta$: (1 : 2) 73.1 ($-\text{OCH}_3$), 25.2, 24.9, 24.6, 24.0 ppm (2 : 3 : 2 : 1, $-\text{CH}_3$).

$\text{K}[\text{S}_2\text{P(O-iso-C}_6\text{H}_11)_2]$, $\delta$: (1 : 2) 73.0, 72.8, 70.5, 69.9 (1 : 1 : 1 : 1, $-\text{OCH}_3$), 27.0, 26.7, 26.3, 25.4, 25.0, 24.1 ppm (1 : 1 : 2 : 6 : 2 : 4, $-\text{CH}_3$).

EPR spectra were recorded on a 70-02 XD/1 radio spectrometer ($\sim$9.5 GHz) at $-295$ K. The operating frequency was measured with a ChZ-46 microwave frequency meter. $g$ Factors were calculated with reference to DPPH. The error in the determination of $g$ factors was $\pm 0.002$: the constants of the hyperfine (HFS) and extra hyperfine structures (EHFS) are quoted in oersteds (Oe) to within $\pm 2\%$. EPR spectra were modeled to the second order of perturbation theory with the WIN- EPR SimFonia program (Bruker software, version 1.2).

Factors, HFS and EHFS constants, resonance line widths, and percent contributions from the Lorentzian and Gaussian functions to the line shapes were variables of the modeling.

$^{13}$C, $^{31}$P, and $^{195}$Pt MAS NMR spectra were recorded on a CMX-360 spectrometer operating at 90.52, 145.72, and 76.99–77.22 MHz, respectively (superconducting magnet with $B_0 = 8.46$ T; Fourier transform). The $^{13}$C–$\text{H}$ and $^{31}$P–$\text{H}$ cross polarization techniques were used; $^{13}$C–$\text{H}$ and $^{31}$P–$\text{H}$ dipolar interactions were suppressed via proton decoupling in a magnetic field with the corresponding proton resonance frequency [5]. Samples ($\sim$300 mg) of the complexes were packed into a zirconia rotor (7.5 mm in diameter). The spinning frequencies in $^{13}$C/$^{31}$P MAS NMR experiments were 4000–5500/3200–5000 (1 Hz). The numbers of scans were 1200–5200/256–400, respectively. The proton $\pi/2$ pulse durations were 5.4/5.4 $\mu$s, respectively. The $^{1}\text{H}$–$^{13}$C/$^{31}$P contact times were 1.5/2.0 ms; the pulses were spaced at 3.0/3.0 s. Isotropic $^{13}$C, $^{31}$P, and $^{195}$Pt chemical shifts $\delta$ (ppm) are referenced to a line of crystalline adamantane [6] used as the external standard ($\delta$ 38.48 ppm relative to tetramethylsilane [7]), 85% $\text{H}_2\text{PO}_4$ (0 ppm) [8], and aqueous 0.1 M $\text{H}_3\text{PtCl}_6$ (0 ppm; the corresponding $^{195}$Pt resonance frequency is 77.3768 MHz) [9], respectively.

In $^{195}$Pt MAS NMR experiments, we used a 60$^\circ$ direct excitation pulse with a 3.7-$\mu$s duration to excite a spectral range of 45 kHz. $^{195}$Pt–$^{1}$H interactions were suppressed via proton decoupling in a magnetic field (amplitude $\gamma B_0/2\pi = 46.9$ kHz) with the corresponding proton resonance frequency (359.945 MHz). The total width of experimental $^{195}$Pt MAS NMR spectra ($\sim$290 kHz) made it impossible to simultaneously excite the entire spectrum at a single carrier frequency. For this reason, we varied the carrier frequency with a step of 77 kHz to excite different regions of the spectrum. The whole pattern was obtained by summation of the individual spectra recorded at 76.991, 77.068, 77.145, and 77.222 MHz. The summation was preceded by shifting the spectra so that the central signal and all sidebands coincided exactly. The spinning frequency was 5000(1) Hz. For each fragment, the number of scans was 20 000 (for I) and 16 800 (for $\beta$-II); the pulses were spaced at 3.0 s. Since the initial region of the free induction decay (FID) diagrams of the MAS NMR spectra was distorted by the decay of the exciting pulse (due to the “ringdown” effect), the distorted range was cut off. To avoid phase distortions of the MAS NMR spectrum, the FID diagram was shifted before Fourier transforms to the decay region by a required number of points. Since the FID diagrams contained over 15 (I) or 27 rotational echoes (II), removal of the initial fragment did not result in critical spectral changes. The magic angle was set by observing the $^{79}$Br resonance frequency of crystalline KBr (90.189 MHz) according to a standard procedure. Its adjustment was performed by minimizing the line widths in the $^{195}$Pt MAS NMR spectrum of natural single-crystal cooperite (PtS), which is characterized by a considerable $^{195}$Pt chemical shift anisotropy ($\delta_{\text{aniso}} = 5873$ ppm, $\eta = 0.37$ [3]) and, consequently, by a high sensitivity of the line width to small deviations of the magic angle.

The width of the reference line for crystalline adamantan (3.5 Hz) was used to check the homogeneity of the magnetic field. The $\delta_{\text{aniso}}$ values were corrected for drift of the magnetic field strength during the measurements (its frequency equivalents for the $^{13}$C/$^{31}$P/$^{195}$Pt nuclei were 0.51/0.11/0.044 Hz/h). The chemical shifts, the integrated intensity ratios for the overlapping signals, and the coupling constants were refined by fragment-by-fragment mathematical modeling of NMR spectra with regard to the line positions and widths and the contributions from the Lorentzian and Gaussian functions to the line shapes. The $^{31}$P chemical shift anisotropy ($\delta_{\text{aniso}} = (\delta_{zz} - \delta_{\text{iso}})$ and the asymmetry parameter of the $^{31}$P chemical shift tensor $(\eta = (\delta_{yy} - \delta_{zz})/(\delta_{zz} - \delta_{\text{iso}}))$ were calculated from diagrams of the $\chi^2$ statistics [10]. Plotting of the diagrams was based on quantitative analysis of the integrated intensity ratios for sidebands (due to spinning) [11, 12] in the spectra recorded at two different spinning frequencies. The calculations were performed with the Mathematica program (version 4.1.2) [13].

Single-crystal X-ray diffraction analysis of complex I was performed on a BRUKER SMART 1000 CCD diffractometer (MoK$_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 173(1) K. Reflections were collected in the hemisphere [14] (crystal–detector