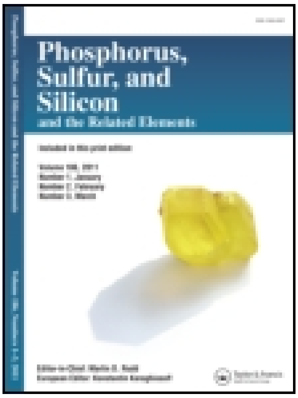

Phosphorus, Sulfur, and Silicon and the Related Elements

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Bis(Tetramethylselenophosphoramidoyl) Methylamine Complexes of Cd(Ii) and Zn(Ii): Synthesis and Multinuclear (^{31}P, ^{77}Se, and ^{113}Cd) Nmr Characterization in Solution

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BIS(TETRAMETHYLSELENOPHOSPHORAMIDOYL) METHYLAMINE COMPLEXES OF Cd(II) AND Zn(II): SYNTHESIS AND MULTINUCLEAR (^{31}P, ^{77}Se, AND ^{113}Cd) NMR CHARACTERIZATION IN SOLUTION

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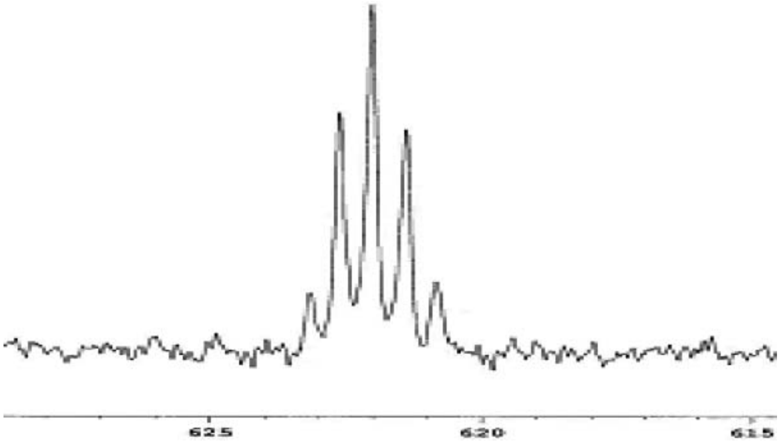
GRAPHICAL ABSTRACT



Abstract *Five new complexes $ZnL_2(ClO_4)_2$ (**1**), $CdL_2(ClO_4)_2$ (**2**), $CdL_2(BF_4)_2$ (**3**), $CdLCl_2$ (**4**), and $CdL(NO_3)_2$ (**5**) [L = $((Me_2N)_2PSe)_2NMe$] have been synthesized and characterized by elemental analysis, infrared (IR) and multinuclear (^{31}P, ^{77}Se, and ^{113}Cd), and nuclear magnetic resonance (NMR) spectroscopy. The ^{31}P and ^{77}Se NMR data showed that the title ligand is coordinated in a bidentate fashion to the metal center via its both P=Se groups. The solution structure of the cadmium complexes was further confirmed by its ^{113}Cd NMR spectra, which displayed a quintuplet for the perchlorate complex and a triplet for each of the nitrate and chloride complexes, respectively due to coupling with four (two ligands) and two (one ligand) equivalent phosphorus nuclei, consistent with a four-coordinate tetrahedral geometry for the cadmium center. The results are discussed and compared with the corresponding oxo and thio analogues.*

Keywords Cadmium complex; zinc complex; Bis(N,N,N′,N′-tetramethylselenophosphoramidoyl)methylamine; ^{31}P, ^{77}Se, and ^{113}Cd NMR

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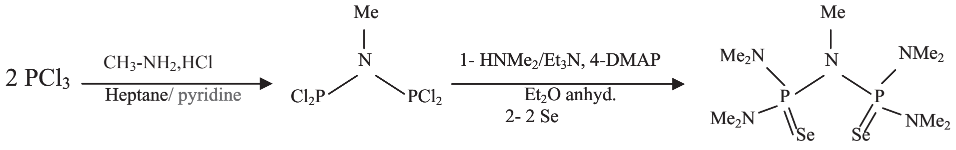
INTRODUCTION

The coordination chemistry of bidentate phosphine chalcogenide ligands of the type $HN[P(E)R_2]_2$ (E = O, S, and Se) has been extensively investigated.[1–3] This has become an active area of research due to the convenient synthetic routes to $HN[P(E)R_2]_2$ and related compounds developed by Woollins et al.[4] These ligands are of interest owing to their use as lanthanide nuclear magnetic resonance (NMR) shift reagents[5] and catalysts.[6] There are, however, relatively few studies on their analogs of the type $RN[P(E)R_2]_2$ (R = alkyl).[7–9] For instance, the nonamethylimidodiphosphoramide, $MeN[P(O)(NMe_2)_2]_2$ (NIPA), has been shown to be an excellent extracting ligand of metal ions and the corresponding complexes with Al, Be, and Cd have been prepared.[8] In a previous work, we reported the preparation and kinetic studies of Cd and Zn complexes with the thio analog, $MeN[P(S)(NMe_2)_2]_2$ (SNIPA).[9] This work is now being extended to the investigation of the diselenide analog, $MeN[P(Se)(NMe_2)_2]_2$ (SeNIPA), and we report here on the synthesis and spectroscopic characterization of new Cd(II) and Zn(II) complexes with this diselenide ligand. The new compounds were characterized by elemental analysis, infrared (IR), and comparison of their NMR data with those related to the free ligand.

RESULTS AND DISCUSSION

Synthesis

The synthesis of $MeN[P(Se)(NMe_2)_2]_2$ was performed using a method previously reported for related systems.[10] The reaction scheme for the ligand preparation is shown in Scheme 1.



Scheme 1

The IR spectrum shows PSe, PNP, and NMe peaks in the expected region (see Experimental section). We have recently reported the X-ray structure of the ligand and showed that it adopts the anticonformation with the P=Se groups rotated with respect to the P–N–P plane.[11]

Treatment of the metal salts in an ethanol solution with the ligand produces complexes **1**–**5**. The new compounds are white solid powders, quite stable and soluble in nitromethane, dichloromethane, and moderately soluble in chloroform. The conductivity measurements show the adducts **4** and **5** to be essentially nonelectrolytes.

The IR spectrum of the ligand shows a strong band at 541 cm^{-1} attributed to $\nu_{P=Se}$. The latter is shifted by $\sim$13 cm^{-1} toward lower wave numbers on coordination to the metal ion. The coordination shift is attributed to a lowering of the P=Se bond order in the complex. This small shift compared with that of P=O and P=S absorptions[12] in the corresponding complexes is reasonable since the vibrations involving the relatively heavy selenium atom would be less sensitive to coordination than those with the lighter phosphorus, oxygen, or sulfur atoms.

Table 1 NMR data (δ (ppm) and J (Hz)) for complexes **1**–**5** and their ligand (L) in CD_2Cl_2

	^{31}P	^{77}Se	^{113}Cd	$\Delta\delta^{31}P$	$\Delta\delta^{77}Se$	$^{1}J_{^{31}P-^{77}Se}$	$^{1}J_{^{31}P-^{13}Cd}$	$^{1}J_{^{113}Cd-^{77}Se}$
L	75.6	−239.6	–	–	–	823.5	–	–
(**1**)	63.5	−119.2	–	12.1	120.4	645.1	–	–
(**2**)	64.3	−152.0	614.3	11.3	87.6	659.9	41.3	322.8
(**3**)	64.2	−150.6	622.1	11.4	89.0	659.9	46.6	297.6
(**4**)	68.4	−161.6	532.4	7.2	78.0	673.1	35.9	–
(**5**)	66.8	−160.6	604.1	8.7	79.1	560.1	–	–

NMR Studies

The multinuclear NMR data (Table 1) indicate the formation of complexes **1**–**5**. For instance, the ^{31}P NMR resonances of bound ligand are shifted to lower frequency compared with those of the free ligand, whereas the ^{77}Se NMR resonances show a higher frequency shift on complexation. The difference in the ^{77}Se chemical shift between free and bound ligands is more important than that observed in ^{31}P NMR spectra. Furthermore, the coupling constant $^{1}J_{P=Se}$ of the free ligand is larger than that of the bound one. Such changes are attributed to a weakening of the P=Se bond upon coordination to the metal atom through selenium.[13]

Although the two-bond P–Cd and the one-bond Se–Cd couplings were observed at ambient temperatures in the ^{31}P and ^{77}Se spectra, the ^{113}Cd showed broad features and the samples were cooled to 188 K to improve resolution. The $^{31}P\{^{1}H\}$ NMR spectra show singlet resonances for each complex (~75% of the total intensity) flanked by two satellites of equal intensities (~12,5% each) arising from the two-bond cadmium–phosphorus coupling, $^{2}J(^{113/111}Cd–^{31}P)$, with weak selenium satellites (Figure 1). In addition, the ^{77}Se NMR

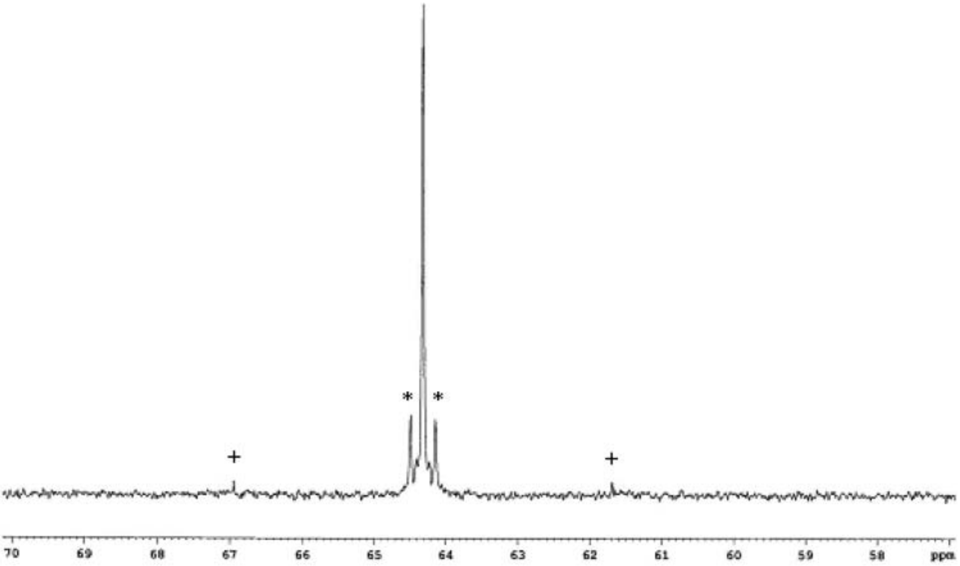


Figure 1 $^{31}P\{1H\}$ NMR spectrum of complex **2** in $CDCl_3$ at 298 K (+ and *: signals related to Se and Cd satellites, respectively).

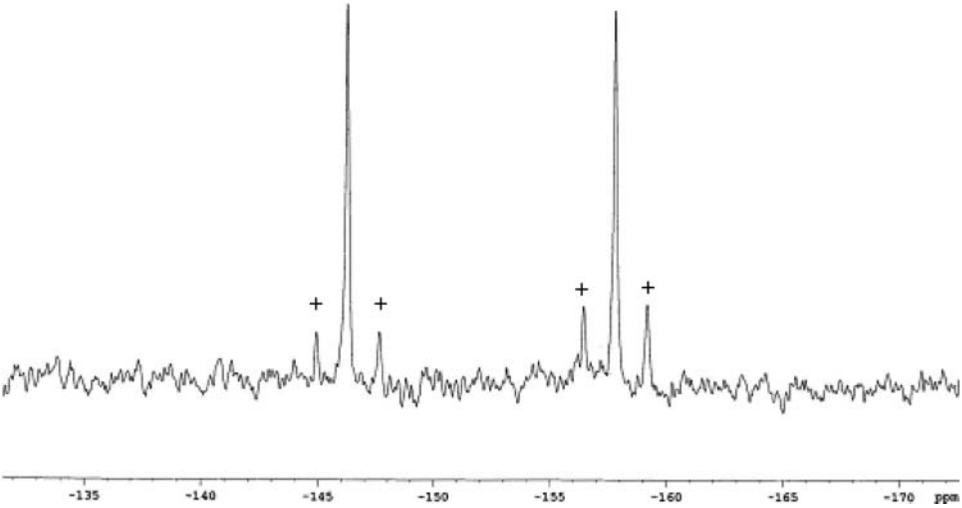


Figure 2 ^{77}Se NMR spectrum of complex **3** in CD_2Cl_2 at 298 K (+: Cd satellites).

spectrum shows for the complex a doublet due to coupling with the phosphorus atom. Each signal of the doublet is flanked by cadmium satellites (see Figure 2). In order to better confirm the structure of these complexes in solution, ^{113}Cd NMR spectroscopy was used.

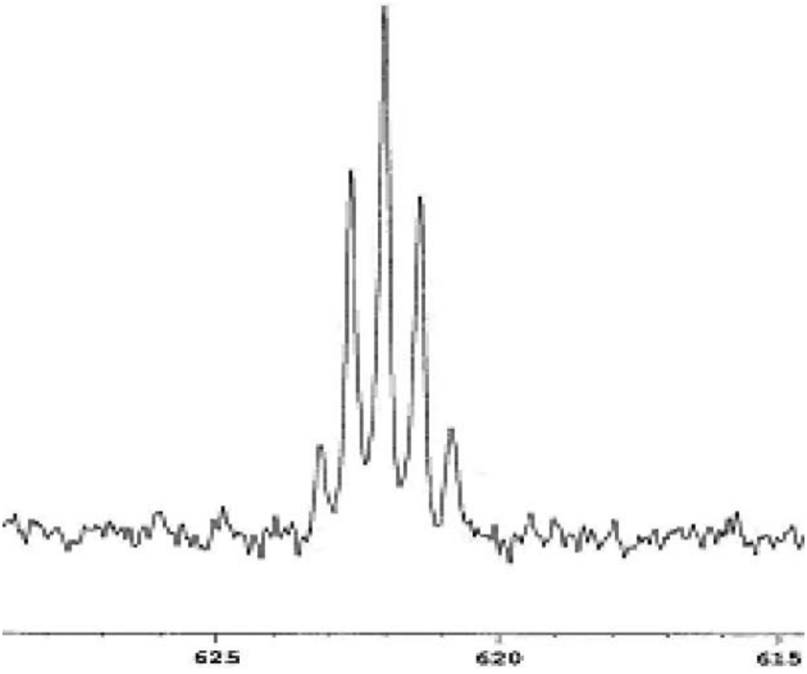


Figure 3 ^{113}Cd NMR spectrum of complex **3** in dichloromethane at 188 K.

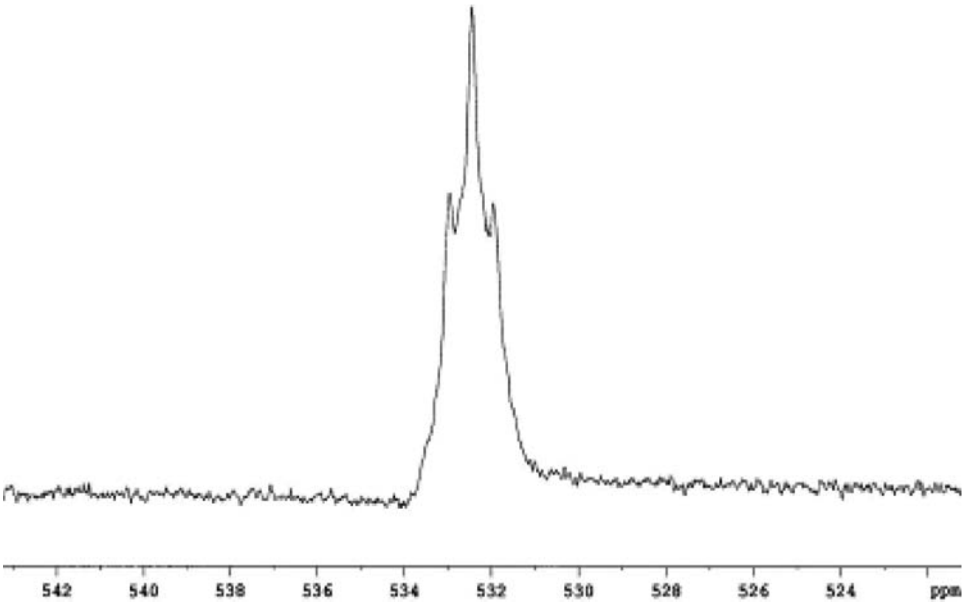


Figure 4 ^{113}Cd NMR spectrum of complex **4** in dichloromethane at 188 K.

The ^{113}Cd NMR spectrum at 188 K (Figure 3) displays a quintuplet for each of the complexes **2** and **3** due to coupling with four magnetically equivalent phosphorus atoms with two-bond ^{113}Cd–^{31}P coupling of $\sim$50 Hz, showing a stoichiometry of $CdL_2(ClO_4)_2$ and $CdL_2(BF_4)_2$. This value compares well with that observed for related cadmium complexes using the monodentate analog $(Me_2N)_3P(Se)$[14] or Ph_3PSe[15] as ligands. Interestingly, the ^{113}Cd NMR spectra show a triplet for each of the complexes **4** and **5** owing to coupling with two phosphorus atoms, consistent with the formula $CdLX_2$ ($X = Cl$ or NO_3) (see Figure 4). Further evidence in support of this assignment is obtained from conductivity measurements, which showed that compounds **4** and **5** are nonelectrolytes in acetonitrile and suggest that both complexes are adducts containing coordinated chlorides and nitrates, whereas complexes **2** and **3** behave as 1:2 electrolytes. This is also confirmed in the IR spectra of **5,** which exhibit strong stretches at 1421, 1390, and 1378 cm^{-1}, in agreement with coordinated O–NO_2[16–18] and those of **2** which show the v(ClO_4) to appear as a sharp single stretch at ca. 1091 and a weak stretch at 620 cm^{-1}. It is worth noting that, when comparing complexes **2**–**5**, the chemical shifts and coupling constants listed in Table 1 suggest that the SeNIPA ligand binds more strongly to the cadmium center than in its corresponding monodentate complex,[14] showing the effect of chelate ring coordination.

The $^2J(^{113}Cd–^{31}P)$ coupling constant for complex **2** is considerably larger than the value measured for the disulfide (SNIPA) analog ($\sim$50 vs. 30 Hz).[9] Such a difference in the metal–phosphorus coupling constant is probably due to the fact that both Se and Cd are big in size whereas there is considerable size difference between S and Cd atoms. This may account for a more important increase in the valence s electron density at the metal nucleus, which would increase the observed $^2J(^{113}Cd–^{31}P)$ value for the SeNIPA complex (**2**) as compared with the SNIPA species. This is also in good agreement with the results obtained for related complexes which showed that the more bulky the ligand the more important the $^{2}J(^{113}\mathrm{Cd}–^{31}\mathrm{P})$ value.[19,20]

CONCLUSION

We have shown that the ligand SeNIPA forms stable chelate complexes with zinc and cadmium ions. The results show that the combination of ^{31}P, ^{77}Se, and ^{113}Cd NMR data in the study of such species is very informative of changes related to complex formation as well as in the elucidation of the structure and composition of metal–ligand coordination compounds. We have also shown that the stability of the selenophosphoryl complexes is comparable to that obtained for sulfur analogs.

EXPERIMENTAL

Materials

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques[21] and stored over molecular sieves.

$Zn(ClO_4)_2\cdot 4H_2O$ (Aldrich) and cadmium salts: perchlorate hydrate (Ventron, 99.9%), $Cd(BF_4)_2\cdot 4H_2O$ (Aldrich, Steinhem, Germany), nitrate tetrahydrate (Fluka, Germany, 99%), and chloride anhydrous (Merck, Darmstardt, Germany, 99%) were used as received.

Measurements

The NMR spectra were recorded on Brucker AC-300 instrument, equipped with a variable temperature unit B-VT-2000 and two probes, CD_2Cl_2 were used as solvent; ^{31}P at 121 MHz (85% H_3PO_4–D_2O), ^{77}Se at 57.2 MHz (Me_2Se), and ^{113}Cd at 66.5 MHz (aq. $Cd(NO_3)_2$, 2 M).

The IR spectra were recorded on a Brucker ISS 66 v/S spectrometer. The conductivity measurements were carried out for 10^{-3} M solutions of the complexes dissolved in acetonitrile (dried on molecular sieves).

Preparation of the Ligand[11]

To a stirred mixture of Me_2NH (14.4 g, 0.32 mol), Et_3N (32.67 g, 0.32 mol) and 4-DMAP (1.58 g, 0.013 mol) in anhydrous diethyl ether (250 mL) cooled at −10 °C was added dropwise $(Cl_2P)_2NMe$[22–24] (19 g, 0.08 mol) in the same solvent (10 mL). The reaction was kept at −10 °C for 10 h then left overnight at room temperature. After removal of the ammonium salt and evaporation of solvent, the oil obtained was dissolved in acetonitrile and cooled to 0 °C, and then selenium (12.8 g, 0.16 mol) was added. The reaction mixture was stirred for 1 h at room temperature and filtered to remove excess Se. The solvent was evaporated to give the product $[(Me_2N)_2PSe]_2NMe$ as an oil, which solidified on cooling. This was found to be pure as shown by its ^{31}P and ^{77}Se NMR spectra. Yield 62%, IR (KBr): $\nu_{P=Se}$ (541 cm^{-1}).

Preparation of Complexes

Zn(Se-NIPA)$_2$(ClO$_4$)$_2$ (1). The complex was prepared in the solid state from the hydrated zinc perchlorate and the ligand in the presence of triethylorthoformate following a method first described by Van Leeuwen and Groeneveld.[25] The hydrated zinc perchlorate (0.30 g, 1.25 mmol) was dissolved in ethanol (30 mL) and an appropriate quantity of triethylorthoformate. After 2 h, a stoichiometric amount of the ligand (1.06 g, 2.50 mmol) was added. The white solid obtained was washed with diethyl ether and dried in vacuo.

Melting points (168.8–170 °C) Anal. calcd. for $C_{18}H_{54}ZnCl_2N_{10}O_8P_2Se_2$: C, 19.38; H, 4.84; N, 12.56. Found: C, 19.11; H, 4.93; N, 12.72. IR (KBr): $\nu_{P=Se}$ (528 cm^{-1}). $\Lambda_M = 290$ cm^2 Ω^{-1} mol^{-1}.

Cd(Se-NIPA)$_2$(ClO$_4$)$_2$ (2). *Note: Caution: cadmium perchlorate is potentially explosive and should be handled in small quantities with extreme care!*

This complex was prepared and purified in the same manner as complex (**1**) from the cadmium salt $Cd(ClO_4)_2 \cdot 4H_2O$ and the title ligand. Melting points (210.0–210.2 °C). Anal. calcd. for $C_{18}H_{54}CdCl_2N_{10}O_8P_2Se_{2:}$ C, 18.59; H, 4.64; N, 12.05. Found: C, 18.41; H, 4.33; N, 12.32. IR (KBr): $\nu_{P=Se}$ (529 cm^{-1}), $\nu_{Se–Cd}$ (321 cm^{-1}). $\Lambda_M = 310$ cm^2 Ω^{-1} mol^{-1} in CH_3CN.

Cd(Se-NIPA)$_2$(BF$_4$)$_2$ (3). Complex **3** was prepared and purified in the same manner as complex (**1**) from the cadmium salt $Cd(BF_4)_2 \cdot 4H_2O$ and the title ligand. The complex was recrystallized from dichloromethane to obtain a white crystalline solid. Yield 60%. Melting points (144.0–144.2 °C) Anal. calcd. for $C_{18}H_{54}CdN_{10}P_4Se_4B_2F_8$: C, 19.01; H, 4.75; N, 12.32. Found: C, 18.95; H, 4.61; N 12.11. IR (KBr): νP=Se (528 cm^{-1}); νCd–Se (323 cm^{-1}). $\Lambda_M = 270$ cm^2 Ω^{-1} mol^{-1} in CH_3CN.

Cd(Se-NIPA)Cl$_2$ (4). To a stirred solution of cadmium chloride (0.40 g, 2.20 mmol) in ethanol (30 mL), a solution of Se-NIPA (0.93 g, 2.20 mmol) was added dropwise. The reaction mixture was stirred for 3 h. The white solid obtained was washed with diethyl ether and dried in vacuo. Yield 1.21 g (82%). Melting points (189.0–189.1 °C). Anal. calcd. for $C_9H_{27}CdCl_2N_5P_2Se_2$: C, 17.75; H 4.43; N, 11.50. Found: C, 17.82; H, 4.38; N 11.42. IR (KBr): νP=Se (524 cm^{-1}); νCd–Se (321 cm^{-1}). $\Lambda_M = 35$ cm^2 Ω^{-1} mol^{-1} in CH_3CN.

Cd(Se-NIPA)(NO$_3$)$_2$ (5). This complex was prepared and purified in the same manner as for complex **4**; yield 67%. Melting points (191.7–191.9 °C) Anal. calcd. for $C_9H_{27}CdN_7P_2Se_2O_6$: C, 16.32; H, 4.08; N, 14.81. Found: C, 16.45; H, 4.31; N 15.02. IR (KBr): νP=Se (527 cm^{-1}); νCd–Se (322 cm^{-1}). $\Lambda_M = 64$ cm^2 Ω^{-1} mol^{-1} in CH_3CN.

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