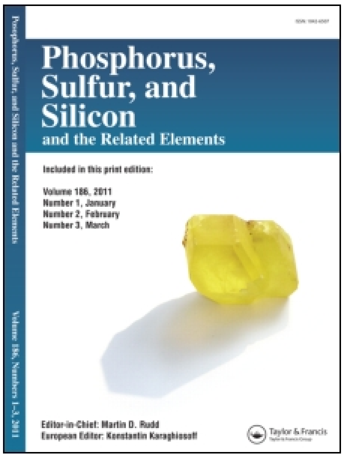

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Tris(dimethylamino)phosphine Selenide Complexes of Cadmium(II): Synthesis and Multinuclear (^{31}P, ^{77}Se, and ^{113}Cd) NMR Characterization in Solution

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To cite this Article Dhia, M. T. Ben , Sanhoury, M. A. M. K. , Zenati, C. and Khaddar, M. R.(2009) 'Tris(dimethylamino)phosphine Selenide Complexes of Cadmium(II): Synthesis and Multinuclear (^{31}P, ^{77}Se, and ^{113}Cd) NMR Characterization in Solution', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 11, 3082 — 3089

To link to this Article: DOI: 10.1080/10426500802704183

URL: http://dx.doi.org/10.1080/10426500802704183

Phosphorus, Sulfur, and Silicon, 184:3082–3089, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802704183

Tris(dimethylamino)phosphine Selenide Complexes of Cadmium(II): Synthesis and Multinuclear (^{31}P, ^{77}Se, and ^{113}Cd) NMR Characterization in Solution

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The complexes $CdL_4(ClO_4)_2$ *(**1**),* $CdL_2(NO_3)_2$ *(**2**), and* CdL_2Cl_2 *(**3**) (L =* $(Me_2N)_3P(Se)$*) have been prepared and characterized by elemental analysis, conductivity measurements, IR, and multinuclear (^{31}P, ^{77}Se, and ^{113}Cd) NMR spectroscopy. ^{31}P and ^{77}Se NMR data were informative of changes associated with complex formation. The structure of the prepared complexes was further confirmed in solution by their ^{113}Cd NMR spectra, which show a quintuplet for the perchlorate complex and a triplet for each of the nitrate and chloride complexes due, respectively, to coupling with four and two equivalent phosphorus atoms, consistent with a four coordinate tetrahedral geometry for the cadmium center. The NMR data are discussed and compared with those reported for related complexes.*

Keywords Cadmium complex; $^{2}J_{P\text{-}Se}$ coupling; ^{31}P, ^{77}Se, and ^{113}Cd NMR; phosphine selenide

INTRODUCTION

The coordination chemistry of phosphorus based ligands bearing the P(E) group (E=O, S, or Se) continues to attract attention because of their selective complexation properties towards "hard/soft" metal ions.[1] The cadmium–selenium complexes may provide the basis for remarkable, well-established,[2–4] protective effect of certain selenium compounds against cadmium intoxication. Furthermore, the Cd-Se bond is an ideal candidate for NMR studies, since both ^{77}Se (7.6% natural abundance) and ^{113}Cd (12.3% natural abundance) have spin I = 1/2, and their resonances are readily accessible with modern NMR instrumentation. Many works have been reported on studies with bidentate

Received 14 July 2008; accepted 18 December 2008.

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ligands, especially of the type $HN[P(E)R_2]_2$ (E=O, S, or Se).[5] However, the chemistry of the monodentate ligands is rather less explored.[6–9] Our interest focuses on the coordination chemistry of monodentate phosphine chalcogenide ligands of the type $R_3P(E)$ towards hard[10] and soft[11] metal ions and the influence that might arise from the presence of the chalcogenide atoms and/or the different substituents attached to the phosphorus atoms of the ligand.[12] Here we describe the synthesis and multinuclear (^{31}P, ^{77}Se and ^{113}Cd) NMR studies of cadmium complexes with tris(dimethylamino)phosphine selenide (TDPSe). The new compounds are characterized by elemental analysis, IR, and comparison of their NMR data with those related to the free ligand.

RESULTS AND DISCUSSION

Synthesis

The addition of the ligand to an ethanol solution of the cadmium salt produces complexes **1–3**. These are white solid powders, which are quite stable and decompose above 200°C. Complexes **1** and **2** are soluble in nitromethane, dichloromethane, and chloroform, whereas complex **3** is soluble in ethanol and nitromethane and is partially soluble in dichloromethane, but is completely soluble in a mixture of dichloromethane and the free ligand. The conductivity measurements show the adducts **2** and **3** to be essentially non-electrolytes.

IR Studies

The infrared spectrum of the ligand shows a strong band at 529 cm^{-1} (vs. 530 cm^{-1})[7] attributed to $\nu_{P=Se}$. The latter is shifted by $\sim$10 cm^{-1} towards lower wave numbers upon coordination to the selenium atom. The coordination shift is attributed to a lowering of the P=Se bond order in the complex. This small shift compared to that of P=O and P=S absorptions[13] 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. Other important vibrational bands observed in IR spectra at 1421, 1390, and 1378 cm^{-1} for **2** are attributed to coordinated O-NO_2 in agreement with literature results[14–16] and at ca. 1091 with a weak stretch at 620 cm^{-1} for **1** assigned to v(ClO_4).

NMR Studies

The ^{31}P and ^{77}Se NMR spectra of the three complexes prepared are quite similar, and the data obtained from these spectra are summarized

TABLE I NMR Data (δ/ppm and J/Hz) for Complexes 1–3 and Their Ligand TDPSe in CD_2Cl_2 at 188 K

Compound	δ_{31P}	δ_{77Se}	δ_{113Cd}	$^1J_{P\text{-}Se}$	$^2J_{P\text{-}Cd}$
TDPSe	82.2	−326	–	786	–
1	71.00	−225	391	633	49.50
2	71.30	−249	388	618	50.27
3[a]	71.50	−250	385	634	40.57

[a] Data obtained by dissolving complex **3** in a mixture of CH_2Cl_2 and free TDPSe.

in Table I. For instance, the ^{31}P NMR resonances of bound ligands are shifted to lower frequency compared with those of the free ligand, whereas the ^{77}Se NMR resonances show a higher frequency shift upon 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 $^1J_{P\text{-}Se}$ of the free ligand is larger than that of the bound one. Such changes are attributed to a weakening of the secondary p_π-d_π bond between the selenium and phosphorus atoms upon coordination to the metal atom through selenium.[17]

A dichloromethane solution of each complex gives, at 298 K, a ^{113}Cd resonance having $\delta_{113Cd} = 350$–400 ppm but no observable ^{113}Cd-^{31}P coupling and a single, broad ^{31}P resonance with $\delta_{31P} = 74$–75 ppm shielded by ∼8 ppm from the comparatively sharp resonance of the free ligand. This shows that free-bound ligand exchange is fast on the NMR time scale at 298 K in this system. At reduced temperature, ligand exchange in these solutions is slow on the NMR time scale: at 202 K, two ^{31}P resonances in complex **1**, for example, are observed—one at 82.2 ppm corresponding to the free ligand and the other ^{31}P resonance (∼75% of the total intensity) at ∼71 ppm is flanked on the one hand by two satellites of equal intensities (∼12,5% each) arising from the two-bond cadmium-phosphorus coupling [$^2J(^{113/111}Cd\text{-}^{31}P) = 49.5$ Hz] and on the other hand by two selenium satellites (with $^1J_{P\text{-}Se} = 633$ Hz). Each of the latter is in turn accompanied by the same cadmium satellites flanking the main signal (see Figure 1). In order to better confirm the structure of these complexes in solution, ^{113}Cd NMR spectroscopy was used.

The ^{113}Cd NMR spectrum at 188 K shows a quintuplet for complex **1** due to coupling with four magnetically equivalent phosphorus atoms with two-bond ^{113}Cd-^{31}P coupling of ∼50 Hz, showing a stoichiometry of $CdL_4(ClO_4)_2$. This value compares well with that observed for related cadmium complexes using Ph_3PSe as ligand.[18] Interestingly, the ^{113}Cd

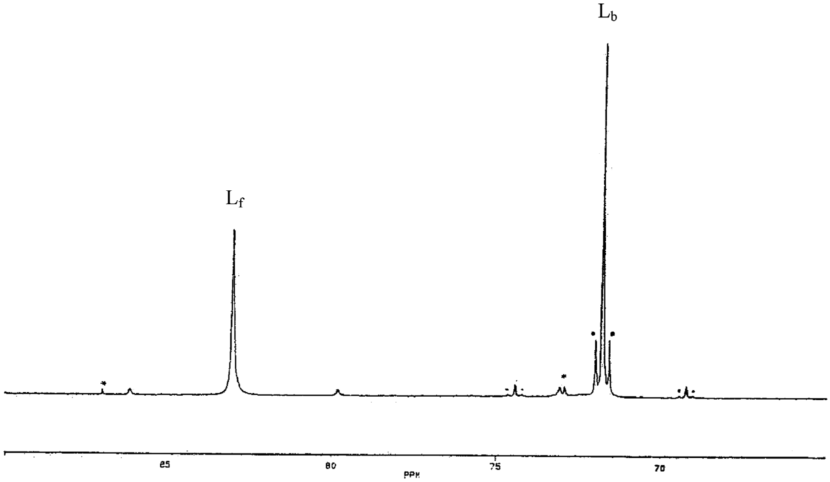

FIGURE 1 $^{31}P\{^{1}H\}$ NMR spectrum of complex **1** in a mixture of dichloromethane and free ligand at 202 K (L_f and L_b : signals related to free and bound ligands respectively;.: Cd satellites and * : impurity).

NMR spectra show a triplet for each of the complexes **2** and **3**, owing to coupling with two phosphorus atoms, consistent with the formula $CdL_2\times_2$ (X=Cl or NO_3) (see Figure 2). Further evidence in support of this assignment is obtained from conductivity measurements, which showed that compounds **2** and **3** are non-electrolytes in nitromethane and suggest that both complexes are adducts containing coordinated chlorides and nitrates, whereas complex **1** behaves as a 1:2 electrolyte. This is also confirmed in the IR spectra of **2**, which exhibits strong stretches at 1421, 1390, and 1378 cm^{-1}, in agreement with coordinated $O\text{-}NO_2$[14–16] and those of **1**, 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 with the same stoichiometry, $CdL_2\times_2$ (i.e., **2** and **3**), the chemical shifts and coupling constants listed in Table I suggest that the TDPSe ligands in complex **2** bind more strongly to the cadmium center than in complex **3**.

The $^{2}J(^{113}Cd\text{-}^{31}P)$ coupling constant for complex **1** is considerably larger than the value measured for the tris(dimethylamino)phosphine sulfide (TDPS) analogue (~50 vs. 30 Hz).[11] 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 in 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 $^{2}J(^{113}Cd\text{-}^{31}P)$ value for the TDPSe complex

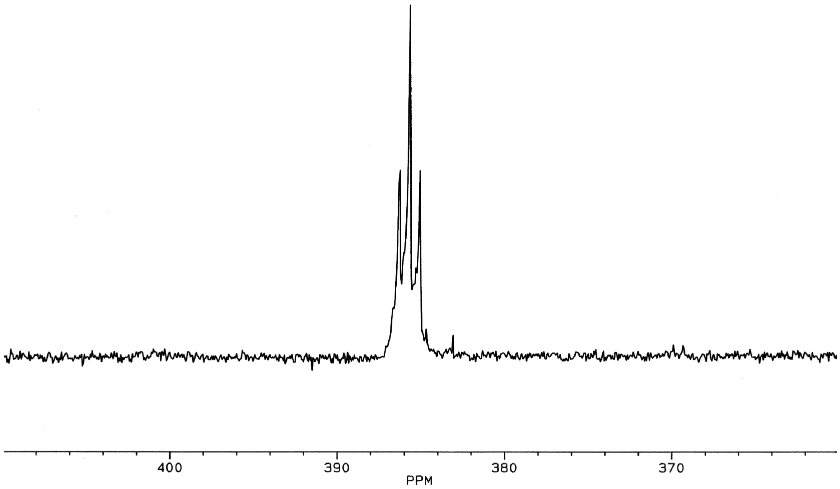

FIGURE 2 ^{113}Cd NMR spectrum of complex **3** in dichloromethane at 188 K.

(**1**) as compared to the TDPS 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 $^{2}J(^{113}Cd\text{-}^{31}P)$ value.[18,19]

CONCLUSION

We have shown that the ligand TDPSe forms stable complexes with the cadmium ion. The results show that 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 analogues. This further indicates that cadmium and selenium can be used as substitutes for zinc and sulfur, respectively, in NMR studies of the coordination environments of the active site in zinc metalloproteins,[23] which are frequently coordinated through the sulfur-containing cysteine and histidines.[24–26]

EXPERIMENTAL

Materials and Measurements

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques[20] and stored over molecular sieves. The NMR spectra were recorded on a Bruker AC-300 instrument in

CD_2Cl_2 as the solvent; ^{31}P at 121 MHz (85% H_3PO_4), ^{1}H at 300 MHz (TMS), ^{113}Cd at 66.5 MHz [aq. $Cd(NO_3)_2$, 2M], and ^{77}Se at 57.2 MHz (Me_2Se). IR spectra: Perkin Elmer Paragon 1000 PC.

Cadmium salts: perchlorate hydrate (Ventron, 99.9%), nitrate tetrahydrate (Fluka, 99%), and chloride anhydrous (Merck, 99%) were used as received.

The ligand $(Me_2N)_3P(Se)$, TDPSe, was prepared according to a method described in the literature.[21] The purity of the products prepared was controlled by ^{31}P and ^{77}Se NMR. The conductivity measurements were carried out for 10^{-3} M solutions of the complexes dissolved in nitromethane (dried on molecular sieves).

Preparation of Complexes

$Cd(TDPSe)_4(ClO_4)_2$ (1)

Note: Caution: cadmium perchlorate is potentially explosive and should be handled in small quantities with extreme care!

Complex **1** was prepared in the solid state from the hydrated cadmium perchlorate and the ligand in the presence of triethylorthoformate following a method first described by Van Leeuwen and Groeneveld.[22] The hydrated cadmium perchlorate was dissolved in ethanol, and an appropriate amount of triethylorthoformate was added. After 2 h, the stoichiometric amount of the ligand was added, and the solution was then concentrated by distilling off the solvent at reduced pressure. Addition of anhydrous ether led to the precipitation of the complex. This was collected, washed with dry diethyl ether, and recrystallized from ethanol:acetonirile (20:80%) to obtain a white crystalline solid. Yield 60%. *Anal.* Calc. For $C_{24}H_{72}CdCl_2N_{12}O_8P_4Se_4$: C, 22.52; H, 5.67; N, 13.13. Found : C, 22.32; H, 5.49; N 13.23. IR (KBr) : $\nu_{P=Se}$ (520 cm^{-1}); $\nu_{Cd\text{-}Se}$ (313 cm^{-1}).

$Cd(TDPSe)_2(NO_3)_2$ (2)

This complex was prepared and purified in the same manner as for complex **1**; yield 67%. Mp (decomp. >200°C) *Anal.* Calc. For $C_{12}H_{36}CdN_8O_6P_2Se_2$: C, 20.00; H 5.03; N, 15.55. Found: C, 19.82; H, 5.44; N 15.68. IR (KBr) : $\nu_{P=Se}$ (523 cm^{-1}); $\nu_{Cd\text{-}Se}$ (312 cm^{-1}).

$\Lambda_M = 13.6\ cm^2\ \Omega^{-1}\ mol^{-1}$ in CH_3NO_2.

$Cd(TDPSe)_2Cl_2$ (3)

To a stirred solution of cadmium chloride (0.40 g, 2.20 mmol) in ethanol (30 mL), a dichloromethane solution (5 mL) of TDPSe (1.07 g, 4.40 mmol) was added dropwise. The reaction mixture was stirred for

3 h, and the solvent was evaporated in vacuo. The white solid obtained was washed with diethyl ether and dried in vacuo. Yield 1.21g (82%). Mp (decomp. >205°C) *Anal.* Calc. For $C_{12}H_{36}CdCl_2N_6P_2Se_2$: C, 21.59; H, 5.43; N, 12.59. Found: C, 21.62; H, 5.61; N 12.42. IR (KBr) : $\nu_{P=Se}$ (519 cm^{-1}); $\nu_{Cd\text{-}Se}$ (312 cm^{-1}). $\Lambda_M = 4.80$ cm^2 Ω^{-1} mol^{-1} in CH_3NO_2.

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