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Mixed Ligand Complexes Containing β-Diphosphoramides. I. Substitution of DMSO by NIPA in Solvates of Cd(II). A Cadmium-113 NMR Study

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Abstract

The stepwise substitution of DMSO in the complex $[Cd(DMSO)_6]^{2+},2ClO_4^-$ on addition of nonamethylimidodiphosphoramide (NIPA) has been monitored by ^{113}Cd NMR at −22 °C in nitromethane solution. All the species $[Cd(DMSO)_{6-2i}(NIPA)_i]^{2+}$ ($i = 0$–3) can be observed as separate signals under these conditions and identified on the basis of signal multiplicity, due to ^{31}P–^{113}Cd coupling. The integration of the signals yields the relative concentrations of the different complexes and allows the determination of the stability constants β_i corresponding to the equilibria

$$[Cd(DMSO)_6]^{2+} + iNIPA \overset{\beta_i}{=} [Cd(DMSO)_{6-2i}(NIPA)_i]^{2+} + 2iDMSO$$

for different ratios of $R = [NIPA]_0/[Cd^{2+}]_0$. The values obtained are $\log \beta_1 = 3.58$, $\log \beta_2 = 6.58$, and $\log \beta_3 = 8.13$. The distribution of the complex species has been calculated for a range of $0 < R < 5$ using these data.

The ^{113}Cd shielding found for the compound $Cd(NIPA)_3^{2+}$ is one of the strongest reported to date for an ionic cadmium complex containing small neutral ligands.

Introduction

The great chemical shift dispersion of ^{113}Cd (>800 ppm) compared to other magnetically active spin $\frac{1}{2}$ nuclei which reflects the sensitivity of this nucleus (and the isotope ^{111}Cd as well) to changes in its local environment makes it a valuable tool in the elucidation of the structure and composition of metal–ligand coordination compounds. Many studies on biological samples, especially metalloproteins, using $^{113}Cd^{2+}$ as a probe able to substitute Zn^{2+} and Ca^{2+} in their binding-sites have been reported in the literature [1]. However, a simple correlation of chemical shifts with structural changes in the complexes is rarely obtained and more data are needed to better understand the factors determining the ^{113}Cd shifts.

The observation of scalar coupling with other spin $\frac{1}{2}$ nuclei often allows us to deduce directly the number of ligands bound to the cadmium ions and the mode of binding, e.g. monodentate or bidentate coordination.

In previous papers [2a–c] we had studied the complexation of di- and tervalent ions by the bidentate organophosphorus ligand nonamethylimidodiphosphoramide, $[(Me_2)_2P(:O)]_2NMe$ (NIPA) and some other compounds of similar structure [3a, b]. The complexes formed between these ligands and the metal ions are very stable kinetically. Little was known however about their thermodynamic stability in the presence of other ligands.

In the following we describe the results obtained for the substitution, on the central Cd^{2+} ion, of a currently used ligand, dimethylsulfoxide (DMSO), by NIPA in an inert medium, nitromethane, giving rise to a series of complexes of formula $[Cd(DMSO)_{6-2i}(NIPA)_i]^{2+}$.

Most of the time, the observation, in mixed ligand systems, of separate NMR signals for the different species at equilibrium in solution is restricted to complexes containing ions with high surface charge densities such as Be(II) [4a, b], Al(III) [5a–g], Ga(III) [6], Y(III) [7], Ti(IV) [8], Zr(IV), Hf(IV), Ce(IV), Th(IV) [9] and/or anionic mono or multidentate ligands [10a–c].

In our case, the strong metal–ligand interactions and the abovementioned NMR properties of the ^{113}Cd nucleus allowed the direct observation of all complex species in a system consisting of a divalent ion and electrically neutral ligands. In the literature, only a few of these systems are known for which at least some of the species present could be distinguished using ^{113}Cd NMR [11a–c].

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Experimental

Materials

The complex $[Cd(DMSO)_6](ClO_4)_2$ was synthesized in the solid state following a procedure first described by VanLeeuwen and Groeneveld [12], from hydrated cadmium perchlorate, $Cd(ClO_4)_2 \cdot 6H_2O$ (ALFA-VENTRON, 99.9% purity), analytical grade DMSO (MERCK Uvasol) and methylorthoformiate in a glove box under an atmosphere of purified argon. **Caution**: all metal perchlorates containing sulphur compounds are potentially explosive and should be prepared in small quantities only. Nonamethylimidodiphosphoramide (NIPA) was obtained by a synthesis described elsewhere [13]. Anhydrous CD_3NO_2 was purchased from C.E.A., Service des Molécules Marquées.

Sample Preparation

Solutions of constant metal concentration but differing in the NIPA/DMSO ratio were prepared by weighing the corresponding amounts of NIPA into a volumetric flask and completing with a 0.328 M solution of $[Cd(DMSO)_6](ClO_4)_2$ in CD_3NO_2. The ligand-to-metal ratios were calculated from the masses of NIPA and the added solution. All samples were prepared under an atmosphere of argon in a glove box.

NMR Spectroscopy

^{113}Cd spectra were recorded on a BRUKER AM 400 spectrometer at 88.76 MHz; the temperature was held constant at -22 °C by the temperature control unit of the spectrometer and by using liquid nitrogen as cooling fluid.

The spectra were taken for samples of natural ^{113}Cd abundance and were not proton decoupled in order to avoid errors in signal areas due to a possible influence of the negative NOE of this nucleus [14]. Line broadening due to proton–cadmium coupling is perceptible only for the signal of $Cd(DMSO)_6^{2+}$ ($\Delta\nu_{1/2} = 10$ Hz), the coupling constant of the NIPA protons, separated from the metal by five bonds (instead of four in the case of DMSO) being very small. All chemical shifts are referenced to 0.1 M aqueous $Cd(ClO_4)_2$; δ values at -22 °C have been measured with respect to $\delta(Cd(NIPA)_3^{2+})$ the shift of which at this temperature with respect to the abovementioned reference had been extrapolated from measurements above 0 °C. Negative shift values indicate increased shielding. The solvent CD_3NO_2 serves as an internal lock substance. Samples are placed in 10 mm o.d. tubes.

Typical acquisition parameters are: 500 scans over 4K points, zero-filled to 16K, sweep width 4000 Hz; 45° pulse; relaxation delay 5 s; quadrature detection. The indicated relaxation delay is sufficient to assure the quantitative determination of the ^{113}Cd containing species.

Results and Discussion

Stabilities

The stepwise substitution of DMSO molecules in the solvate $Cd(DMSO)_6^{2+}$ by the bidentate, electrically neutral ligand NIPA leads to an equilibrium distribution of four complex and two ligand species according to the following scheme [15]

$$[Cd(DMSO)_{6-2(i-1)}(NIPA)_{i-1}]^{2+} + NIPA \overset{K_i}{\rightleftharpoons} [Cd(DMSO)_{6-2i}(NIPA)_i]^{2+} + 2DMSO$$

$(i = 1\text{–}3)$

The overall substitution reaction can be expressed as

$$[Cd(DMSO)_6]^{2+} + iNIPA \overset{\beta_i}{\rightleftharpoons} [Cd(DMSO)_{6-2i}(NIPA)_i]^{2+} + 2iDMSO$$

The corresponding individual equilibrium constants are defined in the usual way as

$$K_i = \frac{[Cd(DMSO)_{6-2i}(NIPA)_i^{2+}] \cdot [DMSO]^2}{[Cd(DMSO)_{6-2i+2}(NIPA)_{i-1}^{2+}] \cdot [NIPA]} \quad (1)$$

$(i = 1, 2, 3)$

and the overall formation constants β_i as the product

$$\beta_i = \prod_i K_i \quad (2)$$

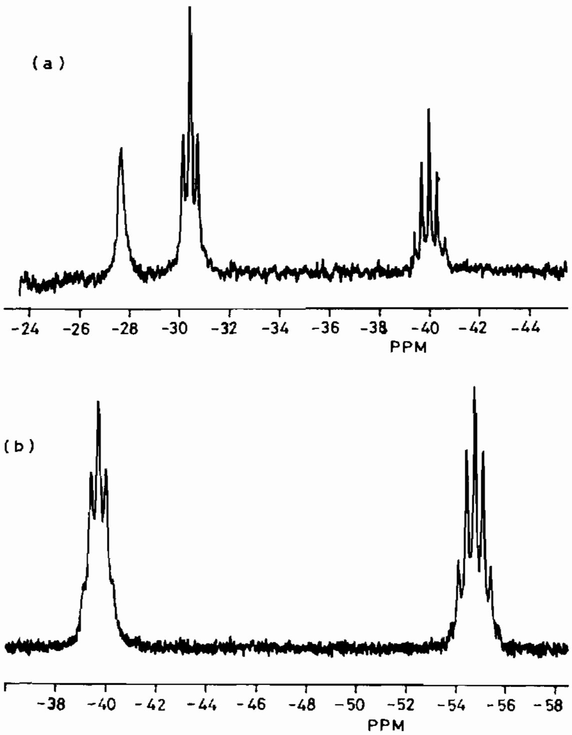

Fig. 1. ^{113}Cd spectra of $Cd(DMSO)_6(ClO_4)_2$ solutions containing different amounts of NIPA at -22 °C. (a) $R = C(NIPA)/C(Cd^{2+}) = 1.02$; (b) $R = 2.00$. Solvent: CD_3NO_2.

The influence of the activity coefficients on the values of the equilibrium constants is supposed to be small and has been neglected in the following, those of the neutral species NIPA and DMSO being supposed close to unity and those of the equally charged cationic species being probably very similar.

Representative spectra for solutions with NIPA/Cd^{2+} ratios of 1 and 2 are shown in Fig. 1a and b.

The different complex species are easily distinguished on the basis of their signal multiplicity. The initial complex $[\mathrm{Cd(DMSO)_6}]^{2+}$ appears as a single line and the species $[\mathrm{Cd(DMSO)_4NIPA}]^{2+}$, $[\mathrm{Cd(DMSO)_2(NIPA)_2}]^{2+}$ and $[\mathrm{Cd(NIPA)_3}]^{2+}$ as a triplet, quintuplet and heptuplet respectively, due to coupling of the corresponding ^{113}Cd nuclei with two, four or six equivalent phosphorus nuclei.

The calculation of the concentrations of all the constituents of the system under study from the peak areas and the mass balance equations

$$C_{\mathrm{M}}{}^0 = \sum_{i=0}^{3} [\mathrm{Cd(DMSO)}_{6-2i}(\mathrm{NIPA})_i{}^{2+}] \qquad (3)$$

$$C_{\mathrm{N}}{}^0 = [\mathrm{NIPA}]_{\mathrm{free}} + \sum_{i=1}^{3} i[\mathrm{Cd(DMSO)}_{6-2i}(\mathrm{NIPA})_i{}^{2+}] \qquad (4)$$

is therefore straightforward.

The concentration of free DMSO is given by eqn. (5)

$$[\mathrm{DMSO}]_{\mathrm{free}} = 6C_{\mathrm{M}}{}^0 - \sum_{i=0}^{2} (6-2i) \times [\mathrm{Cd(DMSO)}_{6-2i}(\mathrm{NIPA})_i{}^{2+}] \qquad (5)$$

The results calculated for different values of $R = C_{\mathrm{N}}{}^0/C_{\mathrm{M}}{}^0$ are summarized in Table I. From the concentrations determined in this way, approximate equilibrium constants were calculated by means of eqn. (1).

A refinement of the initial values was achieved in the following manner. The theoretical distribution of the species as a function of R was computed by using a PASCAL program (COMPFOC1 [16]) and the parameters K_1, K_2 and K_3 were adjusted to fit the experimental points (Fig. 2). Instead of absolute concentrations, the reduced concentrations (or degrees of formation [17]) which are independent of the total metal and ligand concentrations were chosen for the calculations. They are defined as $\alpha_i = C_i/C_{\mathrm{M}}{}^0$ and are related to the overall formation constants β_i and the ratio of free ligand concentrations in the following way

$$\alpha_i = \frac{\beta_i\left(\dfrac{[\mathrm{NIPA}]}{[\mathrm{DMSO}]^2}\right)^i}{\sum\limits_{k=0}^{i} \beta_k\left(\dfrac{[\mathrm{NIPA}]}{[\mathrm{DMSO}]^2}\right)^k} \qquad (6)$$

The α_i values corresponding to the experimental ligand-to-metal ratios R are indicated in Table I in parentheses.

The equilibrium constants before and after refinement are summarized in Table II, together with the logarithms of the formation constants, β_i.

From Fig. 2 it appears that for the system under study, the domains of existence of the different complexes in solution largely overlap. Among the mixed species, the complex containing two NIPA and two DMSO molecules (c) is favoured with respect to $[\mathrm{Cd(DMSO)_4NIPA}]^{2+}$ (b). The concentration of liberated DMSO increases linearly as the added NIPA is taken up practically quantitatively until $R > 2$. For $R > 4$, the tris-chelate complex (d) represents more than 90% of all the solvates present in the system.

The differences between initial and final values of K_1 and K_2 (and consequently of β_i) are mainly

TABLE I. Concentrations $C_i \times 10^2$ (mol/l) of the Different Species and Reduced Concentrations $\alpha_i = C_i/C_{\mathrm{M}}{}^0$ (in brackets) for the Complexes in the System $\mathrm{Cd^{2+}/DMSO/NIPA}$ at Various R ratios and $T = -22$ °C. $C_{\mathrm{M}}{}^0 = 0.328$ mol/l

Species i	C_i (α_i) at $R = C_{\mathrm{N}}{}^0/C_{\mathrm{M}}{}^0$				
	1.02	1.54	2.00	2.52	3.05
DMSO	66.940	98.500	129.800	161.900	183.000
NIPA	0.000	0.000	0.810	1.950	8.470
$[\mathrm{Cd(DMSO)_6}]^{2+}$	8.140 (0.248)	2.100 (0.064)	0.142 (0.004)	0.000 (0.000)	0.000 (0.000)
$[\mathrm{Cd(DMSO)_4NIPA}]^{2+}$	15.850 (0.483)	12.150 (0.370)	4.850 (0.148)	0.185 (0.006)	0.000 (0.000)
$[\mathrm{Cd(DMSO)_2(NIPA)_2}]^{2+}$	8.810 (0.269)	18.550 (0.566)	23.400 (0.713)	17.070 (0.520)	6.870 (0.210)
$[\mathrm{Cd(NIPA)_3}]^{2+}$	0.000 (0.000)	0.450 (0.014)	4.420 (0.135)	15.540 (0.474)	25.900 (0.790)

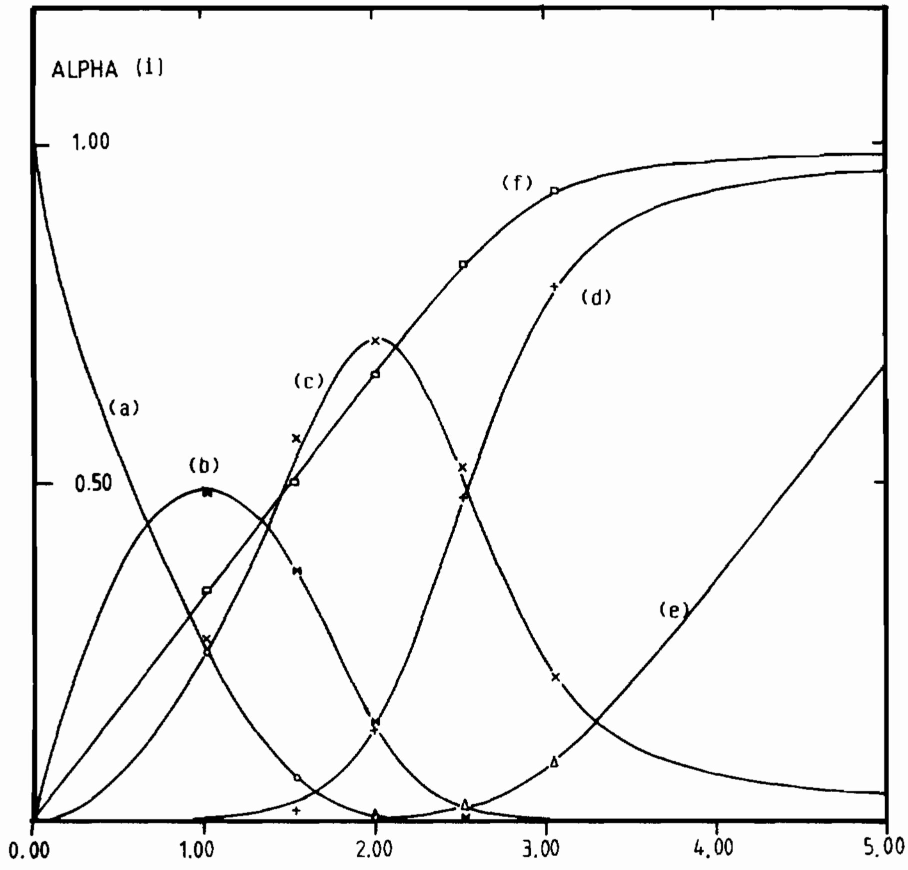

Fig. 2. Calculated distributions and experimentally determined reduced concentrations of the species $[Cd(DMSO)_6]^{2+}$ (a), $[Cd(DMSO)_4NIPA]^{2+}$ (b), $[Cd(DMSO)_2(NIPA)_2]^{2+}$ (c), $[Cd(NIPA)_3]^{2+}$ (d), $[NIPA]_{free}$ (e), and $[DMSO]_{free}$ (f) in the system Cd^{2+}/DMSO/NIPA–CD_3NO_2 at −22 °C. The values of free DMSO and free NIPA have been divided by 6 and 3, respectively, for scaling reasons.

TABLE II. Equilibrium Constants K_i (l mol^{-1}) Before and After Refinement and Logarithms of Formation Constants β_i for the System Cd^{2+}/DMSO/NIPA in Nitromethane at −22 °C

Equilibrium constant	$K_1 \times 10^{-3}$	$K_2 \times 10^{-2}$	$K_3 \times 10^{-1}$	log β_1	log β_2	log β_3
Initial	7.1[a]	10.0[a]	13.6[b]	3.85	6.85	8.99
	±3.6	±0.5	±0.7	±0.30	±0.30	±0.35
Final	3.8	9.9	3.8	3.58	6.58	8.13
	±0.2	±0.15	±0.2	±0.02	±0.02	±0.08

[a] From concentration measurements at $R = 2$. [b] Average value from results for $R = 2.52$ and $R = 3.05$.

due to the uncertainty of the indirectly calculated free NIPA concentrations (eqn. (4)). Relatively small errors in the concentrations of the complexes lead to large variations of the concentrations of this ligand, which is, for $R < 3$, present in small quantities only.

However, the good fit of all calculated curves to all the experimental α_i values corresponding to the concentrations of at least four species at five different R ratios lends a large degree of confidence to the final constants.

The values of the stability constants reflect the strong tendency of NIPA to complex the Cd^{2+} ion by displacing the initially bound DMSO. The chelate character of the complexes formed is one of the reasons for the enhanced stability; on the other hand, the higher donicity of the phosphoryl groups compared to sulphoxides [18] favours the coordination of NIPA to the central ion.

Chemical Shifts

The chemical shift found for the complex $Cd(DMSO)_6^{2+}$, of −27.4 ppm, is close to the value reported by Haberkorn *et al.* for 0.5 M cadmium perchlorate in pure DMSO (−26.0 ppm) [19].

TABLE III. ^{113}Cd Chemical Shifts, δ, and Shift Differences, $\Delta\delta$, for the Complexes $[Cd(DMSO)_{6-2i}(NIPA)_i]^{2+}$ (i = 0–3) in Nitromethane at −22 °C

Complex ion	δ_{Cd} (ppm)[a]	$\Delta\delta_{Cd}$ (ppm)
$[Cd(DMSO)_6]^{2+}$	−27.4	0.0
$[Cd(DMSO)_4NIPA]^{2+}$	−30.2	2.8
$[Cd(DMSO)_2(NIPA)_2]^{2+}$	−39.7	9.5
$[Cd(NIPA)_3]^{2+}$	−54.7	15.0

[a] Relative to 0.1 M aqueous $Cd(ClO_4)_2$ by extrapolation of $\delta(Cd(NIPA)_3^{2+})$ to −22 °C.

The substitution of two, four, and finally six DMSO molecules in the solvation shell of the Cd^{2+} ion results in a considerable shift of the corresponding ^{113}Cd signal to higher field strength as shown in Table III. The increased shielding, however, is not a linear function of the number of organophosphorus or DMSO ligands present in the complexes. Similar observations have been reported by Dean [11a] for the substitution of $R_3P{=}S$ ligands by their selenium analogues in tetrahedral complexes of cadmium. As pointed out by Ellis [20], ^{113}Cd chemical shifts are determined by several important factors; besides the nature of the ligands, the structure and symmetry of the complex species play a major role. The change from octahedral (O_h) symmetry in $Cd(DMSO)_6^{2+}$ to C_{2v} in the mixed species and finally to D_3 in $Cd(NIPA)_3^{2+}$ probably modulates the influence of the increasing shielding due to the replacement of S=O by P=O groups. All shift values encountered in these compounds are characteristic for an environment of six oxygen atoms around cadmium, but the complex ion $Cd(NIPA)_3^{2+}$ presents a particularly high ^{113}Cd shielding for a complex including small ligands, comparable to the cadmium–nitrato complex formed in 4.5 M aqueous solutions of $Cd(NO_3)_2$ (δ = −49.4 ppm) [21].

The observation of only one signal for the complex $[Cd(DMSO)_2(NIPA)_2]^{2+}$ can be explained either by a much greater stability of one of the two possible isomers (*cis* or *trans*) or by a rapid intramolecular exchange of the ligands leading to an averaged NMR signal.

The constant value of the coupling constant ^2J(Cd–P), of 29.9 Hz, along the series of complexes indicates the absence of anion or solvent coordination to the central ion [22].

Conclusions

The system Cd^{2+}/DMSO/NIPA in nitromethane solution is one of the few for which separate ^{113}Cd NMR signals for all the solvate species can be observed at moderately low temperatures, as a consequence of a slow intermolecular ligand exchange. This study permitted us to extract the equilibrium constants for the substitution of DMSO by NIPA with good accuracy. Their values prove the high coordinating power of the ligand NIPA confirming thereby the conclusions drawn from previous kinetic studies. The assignment of the NMR signals to the different complex species was facilitated by the well resolved ^{113}Cd–^{31}P couplings allowing us to deduce directly the number of bound organophosphorus ligands.

The shielding found for the tris-chelate complex $Cd(NIPA)_3^{2+}$ is one of the highest reported in the literature for Cd(II) complexes with small neutral ligands; this is in agreement with the highly ionic nature of the ion–ligand bonds in the NIPA complexes [23]. Higher shieldings have been reported for cadmium–protein complexes [24] and $Cd(AsF_6)_2$ in SO_2 solution [25].

Work is in progress to extend these studies to systems containing other bidentate phosphorylated molecules.

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