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The Solution Behaviour of Nickel(II) Halide Complexes of 1,2-Bis(Diphenylphosphino)Ethane (dpe): The Existence of Five-co-ordinate $[Ni(dpe)_2X]^+$ Species

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Nickel(II) halide complexes with the bidentate ligand 1,2-bis(diphenylphosphino)ethane (dpe) have been reinvestigated, with particular regard to their behaviour in solution. Conclusive evidence of the existence of low-spin five co-ordinate $[Ni(dpe)_2X]^+$ species (X = Cl, Br, I), in equilibrium with cis-*planar $[Ni(dpe)X_2]$ species, is given on the basis of spectrophotometric and conductometric data. Calorimetric measurements suggest that the stability of five-co-ordinate $[Ni(dpe)_2Br]^+$ is comparable to that of the previously reported $[Co(dpe)_2Br]^+$ complex.*

Introduction

In recent years, a number of papers have dealt with the bonding properties of the bidentate ligand 1,2-bis(diphenylphosphino)ethane (dpe) toward nickel(II) and cobalt(II) ions. The types of complexes so far isolated are: (a) ionic five-co-ordinate $[Co(dpe)_2X]Y$ complexes (X = Cl, Br, I; donor set P_4X);[1] (b) non-ionic *cis*-square-planar $[Ni(dpe)X_2]$ (X = Cl, Br, I, NCS, CN; donor set P_2X_2);[2-6] (c) $M(dpe)_2X_2$ complexes (M = Co, Ni; X = ClO_4, CN; M = Ni; X = Br, I, NO_3).[1,4-6] As to type (c) complexes, only the perchlorato and nitrato-derivatives have been attributed a ionic square-planar structure $[M(dpe)_2]X_2$ (donor set P_4) both in the solid state and in solution,[1,4] whereas for complexes $[M(dpe)_2(CN)_2]$ a trigonal bipyramidal structure was suggested with one chelating and one monodentate dpe ligand.[6] For $Ni(dpe)_2X_2$ complexes with X = Br, I, on the other hand, only sparse and not conclusive experimental data have been reported so far. This prompted us to further investigate them, with particular regard to their solution behaviour and to the possible existence of five-co-ordinate $[Ni(dpe)_2X]^+$ species, similar to those isolated with cobalt(II) (type (a)).

Results and Discussion

Reflectance spectra of $Ni(dpe)_2X_2$ complexes (X = Br, I, ClO_4) are reported in Table I). All the spectra are similar in shape, consisting merely of a shoulder around 24.0-24.2 kK on the low-energy side of a strong charge-transfer absorption. However, a square-planar $[Ni(dpe)_2](ClO_4)_2$ structure was attributed to the perchlorato complex, whereas a six-co-ordinate, tetragonally distorted structure was suggested for the halo-complexes, the axial ligand field being weak enough to account for the observed spectral features and the diamagnetism of these complexes.[2-4]

A sharp distinction between the two types of complexes occurs in solution. The perchlorato-complex in non-aqueous solvents maintains the above spectral features and has uni-bivalent electrolyte character (Table I), consistent with the proposed structure, whereas the halo-complexes show a completely different spectrum (one band at 20.8 and 19.2 kK for the bromide and iodide, respectively) and conductivity values lower than those found for uni-univalent electrolytes (Table I). While these results indicate a definite interaction between the halogens and the square-planar $[Ni(dpe)_2]^{2+}$ moiety, no unambiguous explanation has been offered so far. Equilibrium (1) was suggested,[3] on account of the similarity of the absorption spectra to those of $[Ni(dpe)X_2]$ complexes

$$\underset{\text{six-co-ordinate}}{[Ni(dpe)_2X_2]} \rightleftharpoons \underset{\text{square-planar}}{[Ni(dpe)X_2]} + dpe \qquad (1)$$

However, this does not account for the not negligible conductivity of $[Ni(dpe)_2X_2]$ complexes. Furthermore, the spectra of $[Ni(dpe)X_2]$ and $[Ni(dpe)_2X_2]$ slightly but significantly differ in frequency and intensity of the absorption band, which is, in the latter case, asymmetric due to the presence of a shoulder on the low-energy side.

Spectrophotometric and conductometric measurements on nitroethane solutions of $[Ni(dpe)X_2]$ complexes show that on increasing the $C_{dpe}/C_{complex}$ ratio: (a) the absorption band changes in frequency and intensity, more evidently for the iodo- complex (Figure 1), with a simultaneous enhancement of the shoulder

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Table I. Conductometric and spectrophotometric data for complexes.

Compound	Λ [a] (cm^2 ohm^{-1}	State [b]	Absorption max. (kK) with ε_{molar} for soln. in parentheses [c]
(1) $[Ni(dpe)Cl_2]$	—	R	21.9
		N	21.8 (1650)
		N[d]	17.0sh, 21.2 (1670)
(2) $[Ni(dpe)Br_2]$	—	R	21.1
		N	21.0 (1770)
		N[d]	17.0sh, 20.8 (1680)
(3) $[Ni(dpe)I_2]$	—	R	19.2
		N	19.2 (1950)
		N[d]	16.0sh, 19.8 (1360)
(4) $[Ni(dpe)_2Br_2]$	48	R	24.2 sh
		N	17.0sh, 20.8 (1700)
(5) $[Ni(dpe)_2I_2]$	64	R	24.2sh
		N [e]	16.0sh, 19.0 (1580)
(6) $[Ni(dpe)_2](ClO_4)]_2$	131	R	24.0sh
		N	24.1sh

[a] For *ca.* 10^{-3} *M* soln. in nitroethane at 20°. Reference value: $[Bu_4N]Br$, 78. [b] R = Diffuse reflectance, N = nitroethane. [c] sh = shoulder. [d] With excess ligand added. [e] For ca. 8×10^{-4} *M* soln. (concentration depedent).

on the low-energy side, the resulting spectrum being typical for five-co-ordinate square-pyramidal low-spin nickel(II) complexes;[7] (b) the molar conductivity increases toward typical values of uni-univalent electrolytes (Figure 2). Both results are consistent with displacement of one halide ion by one dpe molecule with formation of five-co-ordinate $[Ni(dpe)_2X]^+$ species according to equilibrium (2)

$$\underset{\text{square-planar}}{[Ni(dpe)X_2]} + dpe \rightleftharpoons \underset{\text{five-co-ordinate}}{[Ni(dpe)_2X]} + X^- \qquad (2)$$

The above data also indicate increasing displacement to the right in the order $Cl \ll Br < I$. It is worth remembering that reaction od dpe with $[Ni(dpe)(CN)_2]$ does not result in substitution of a CN group, but in coordination of one more molecule of dpe acting as monodentate.[6]

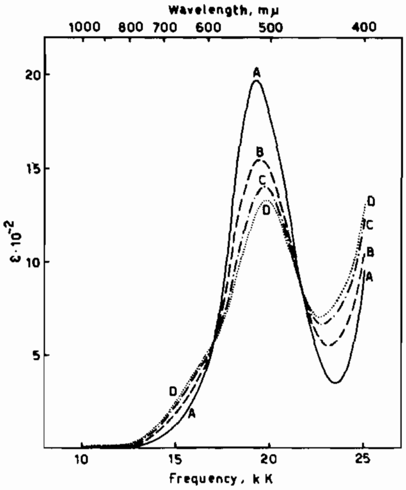

Figure 1. Absorption spectra of nitroethane solutions of $[Ni(dpe)I_2]$, with different ligand/complex ratios. $C_{dpe}/C_{complex}$ ratio: (A) 0.00; (B) 0.52; (C) 1.05; (D) 5.2.

Conductometric dilution studies[8] on $Ni(dpe)_2X_2$ solutions, with excess ligand added, show that the slope of Λ_o–Λ_e *vs.* $\sqrt{C_e}$ curve is in the range for 1:1 electrolytes, thus excluding polynuclear species.

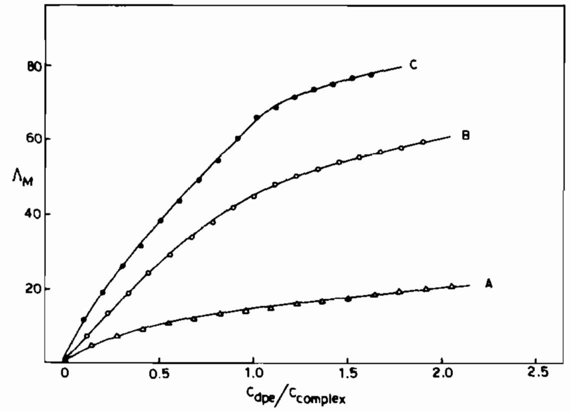

Figure 2. Molar conductivity values of $[Ni(dpe)X_2]$ complexes in nitroethane plotted against $C_{dpe}/C_{complex}$. (X=Cl, curve (A); X=Br, curve (B); X=I, curve (C)).

A virtually complete formation of five-co-ordinate $[Ni(dpe)_2X]^+$ species was evidenced by conductometric and spectrophotometric titrations (Figures 3, 4) of planar $[Ni(dpe)_2](ClO_4)_2$ with $[Bu_4N]X$ halides (X = Cl, Br, I). Both types of curves show a sharp end-point corresponding to 1:1 halide/complex ratio. An amount of ligand sufficient to repress displacement to left of equilibrium (2) was added in each case.

Further evidence is given by the fully similar titration curves obtained with $[Co(dpe)_2](ClO_4)_2$ in the same conditions: as mentioned, five-co-ordinate $[Co(dpe)_2X]^+$ have been characterised also in the solid state.[1]

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An estimation of the relative stability of $[Ni(dpe)_2Br]^+$ and $[Co(dpe)_2Br]^+$ complexes is given by calorimetric measurements of ΔH values relative to reaction (3)

$$\underset{\text{planar}}{[M(dpe)_2]^{2+}} + Br^- \rightleftharpoons \underset{\text{five-co-ordinate}}{[M(dpe)_2Br]^+} \qquad (3)$$

The found ΔH values are 0.0±0.2 and +0.6±0.2 $Kcal/mole^{-1}$ for the nickel and cobalt complex respectively. Upon the assumption that solvation of all the species does not depend on the nature of the M metal, these results indicate that both complexes in solution have practically the same stability, mainly due to entropy terms.

Similar results were also reported for similar equilibria, concerning the formation of five-co-ordinate adducts.[9]

Spectrophotometric dilution studies show that equilibrium (3) is significantly displaced to left with dilution in the case of $[Ni(dpe)_2I]^+$, whereas negligible dissociation is observed for $[Ni(dpe)_2Br]^+$. The stability order, relative to the halides, is thus Br>I.

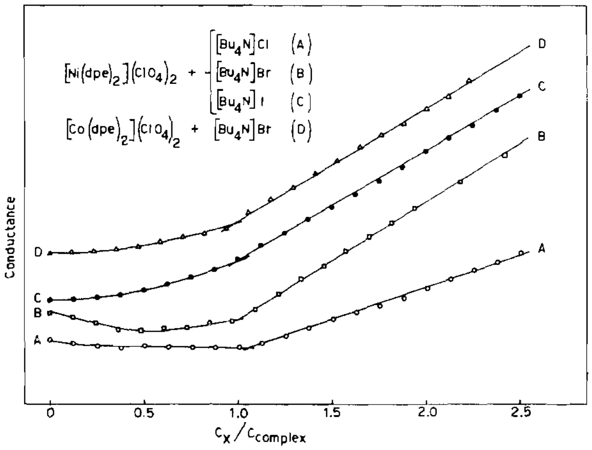

Figure 3. Conductometric titration curves of $[M(dpe)_2](ClO_4)_2$ complexes with $[Bu_4N]X$ halides (X = Cl, Br, I) in nitroethane solutions. Tenfold excess of ligand was added in each case.

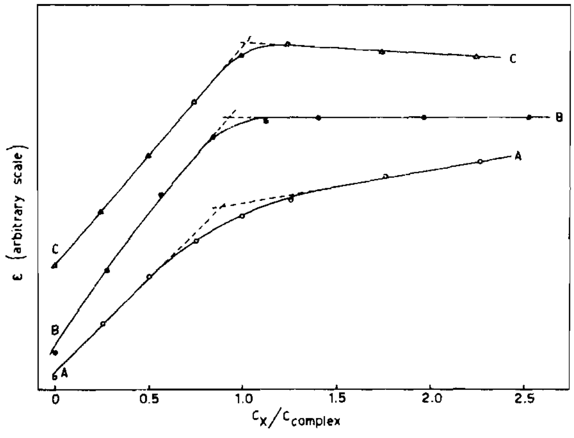

Figure 4. Spectrophotometric titration curves of $[Ni(dpe)_2](ClO_4)_2$ with $[Bu_4N]X$: X = I, curve (A); X = Br, curve (B); X = Cl, curve (C). Tenfold excess of ligand was added in each case.

Conclusions

The present data demonstrate that one of the main species in solution of $Ni(dpe)_2X_2$ complexes is the five-co-ordinate $[Ni(dpe)_2X]^+$ cation, deriving from the dissociation equilibrium (2). This has been identified also with X = Cl, although the isolation of $Ni(dpe)_2Cl_2$ complex has always proved unsuccessful.

Failure to isolate the five-co-ordinate $[Ni(dpe)_2X]^+$ complexes, contrarily to what is found for similar bis-phosphine ligands such as *cis*-1,2-bis(diphenylphosphino)ethylene (VPP)[5] and 1,2-bis(phenylphosphino)ethane (ABPP),[10] was in part ascribed to intrinsic steric hindrance of the dpe ligand.[5] The here reported proofs that such species do exist in solution, however, suggest that solid-state factors are mainly responsible for their non-occurrence in the solid state.

Experimental Section

All materials were reagent grade. The complexes were prepared according to literature methods.[1-4]

Spectrophotometric measurements were carried out with a Beckman DK2A spectrophotometer, using 1-cm. silica cells.

The molar conductivity values were determined at 20°C with a WTW model LBR/B conductance bridge.

Calorimetric measurements were carried out with a LKB 8700/1 reaction calorimeter, using a procedure already described.[11] Experimental details are available and can be had on request from the authors.

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