Coordination Chemistry of Phosphoguanidines, I

Nickel(II) Complexes of 1,3-Bis(di-*N*-propyl-phosphinyl)-guanidine

K. NAG and S. N. BOSE

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta, India

(Z. Naturforsch. **29b**, 542-545 [1974]; received May 2, 1974)

Nickel(II) perchlorate, Chloride complexes, Iodide complexes, Sulfate complexes, Phosphoguanidines

Coordination compounds of some nickel (II) salts derived from 1,3-bis(di-*n*-propyl-phosphinyl)guanidine (DPPG) have been synthesized and characterized from their chemical analyses, infrared spectra, electronic spectra, conductance and magnetic moment measurements. With nickel perchlorate, an octahedral complex of the type $[\text{Ni}(\text{DPPG})_2](\text{ClO}_4)_2$ has been prepared, while with corresponding chloride and iodide square planar compounds of the type $[\text{Ni}(\text{DPPG})\text{X}]\text{X}$ have been obtained. With nickel sulfate a 1:1 diamagnetic complex is formed in which sulfate ion is unidentately bound. In all the complexes DPPG acts as a tridentate ligand and bonding takes place from two $\text{P}=\text{O}$ groups and the imino nitrogen atom. The solvation behavior of the complexes has also been studied.

Current emphasis on studying the donor ability of phosphoryl grouping towards metal ions are amply reflected in a large array of recent publications^{1,2}. To this end, isolation and characterization of metal complexes containing monodentate $\text{P}=\text{O}$ groups have been accomplished with phosphine oxides³⁻¹⁰, phosphoramides^{2,10-17}, neutral phosphates and phosphonate esters¹⁸⁻²¹. Compounds of this type containing bulky substituents have been used as extracting agents²²⁻²³ for many years. Ligands containing two phosphoryl groups separated by methylene linkage derived from phosphonate esters have also found applications in solvent extraction studies^{24,25} and metal complexes have been isolated in several cases²⁶⁻²⁸. In another class of compounds, *viz.* (pyridyl-2-methyl) diphenyl phosphine oxide²⁹ and pyridine-2-phosphonate alkyl esters³⁰ bonding with metal ions takes place from the phosphoryl group and the heterocyclic nitrogen atom. It goes, however, to state that investigations so far are limited to uni- and bidentate type of ligands. In general, with ligands containing the $\text{P}=\text{O}$ grouping, weak metal adducts

are formed. It appears, therefore, that insertion of urea, thiourea and guanidine moiety between two phosphoryl groups would augment the donor capacity of such ligands towards metal ions. With this view we wish to report here the coordination compounds derived from 1,3-bis(di-*n*-propyl phosphinyl)-guanidine (I) of some nickel salts (perchlorate, chloride, iodide and sulphate).

Experimental

Chemicals

Reagent grade (E. Merck) guanidiniumchloride, phosphorous pentachloride and dimethoxy propane were used. Nickel iodide was prepared by refluxing methanolic solution of hydrated nickel chloride with an excess of finely powdered potassium iodide for several hours, reflux continued for some more time after addition of a suitable amount of dimethoxy propane. The solution was concentrated, cooled and filtered. The methanolic solution of nickel iodide was used for compound preparation. Other nickel salts were G. R., E. Merck. Solvents

Requests for reprints should be sent to Dr. K. NAG, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India.

(chloroform, methanol etc.) were purified by standard procedures. Nitromethane was purified by a procedure due to SUTTON³¹.

Synthetic procedure

The ligand (DPPG) was prepared by reacting 0.5 mole of guanidinium chloride with 1.0 mole of phosphorous pentachloride in dry chloroform under nitrogen atmosphere followed by addition of 3.0 moles of *n*-propanol adopting the method of SHERIF³². The ligand was then purified by heating the product at 80 °C under reduced pressure (0.1 mm Hg) for 30 minutes. It is soluble in methanol and chloroform and is a highly viscous oil.

The complexes were prepared by following a generalized procedure. The nickel salt was dissolved in a (1:1) mixture of methanol and dimethoxy propane. To the hot solution (~50 °C), the desired amount of the ligand dissolved in the same solvent mixture was added and the mixture was kept at this temperature for ~1 h. The solution was then evaporated to a small volume, cooled and an excess of chloroform was added. The solvent was decanted off from the crystalline precipitate and the product was purified by repeatedly refluxing with chloroform. In the case of the perchlorate complex, the metal-to-ligand ratio used was 1:3, while for other cases a ratio of 1:1.2 was maintained. The complexes are soluble in polar solvents like water, methanol, ethanol, acetone etc. The iodo complex is soluble in nitromethane, while other complexes are very sparingly soluble in it. All of them are hygroscopic and insoluble in chloroform, benzene etc.

Analysis

Nickel was estimated by customary procedure, nitrogen by semimicro combustion analysis and the anions by dissolving a known amount of the compound in water and liberating the corresponding acid by passing through a cation-exchanger in its hydrogen ion form. Analytical results are given in Table I.

Measurements

IR spectra (Table II), obtained on KBr pellets for the complexes and liquid film for the ligand were recorded in Perkin-Elmer model 21. Electronic spectra (Table III) were obtained from Hilger Uvispek spectrophotometer and Spectro Mom 201. Conductance measurement were carried out with a Philips conductivity bridge (PR 9500/90) and magnetic moments were measured in a Gouy balance.

Results and Discussion

The new nickel complexes described here are either bis-type Ni(DPPG)₂(ClO₄)₂ or mono-type Ni(DPPG)X₂ (X = Cl⁻, I⁻, 1/2 SO₄²⁻). The stoichiometry of their composition depends upon the molar ratio of metal salt and ligand chosen to react.

It appears that DPPG (I) has many possible donor sites (*viz.* two P=O, C=NH, and two NH) for complexing with metal ions. The pertinent IR bands for the ligand and its metal complexes are shown in Table II, from which it is evident that the

Table I. Analysis and some physical properties of nickel(II) complexes.

Compound	Colour	Nickel [%]		Nitrogen [%]		Anion [%]		m.p.* [°C]
		Found	Calcd	Found	Calcd	Found	Calcd	
Ni(DPPG) ₂ (ClO ₄) ₂	Pale green	5.60	5.69	8.24	8.14	19.9	19.29	265
Ni(DPPG)SO ₄	Pale yellow	10.64	10.84	7.85	7.75	17.48	17.72	290
Ni(DPPG)Cl ₂	Pale yellow	11.63	11.36	8.23	8.13	13.54	13.74	270
Ni(DPPG)I ₂	Brick red	8.18	8.39	6.08	6.00	36.09	36.28	225

* Melts with decomposition (uncorrected).

Table II. Pertinent IR*** data for DPPG and its nickel complexes.

DPPG ₃ *	Ni(DPPG) ₂ (ClO ₄) ₂ **	Ni(DPPG)SO ₄ **	Ni(DPPG)Cl ₂ **	Ni(DPPG)I ₂ **	Assignments
3300 s	3290 s	3300 s	3300 s	3280 s	N—H stretch
—	3200 m	—	3200 m	3210 w	
3100 s	3100 m	3060 m	3100 m	3080 m	N—H (imino)
1660 s	1645 s	1650 s	1650 s	1645 s	N—H deform.
1590 m	1575 m	1570 m	1575 m	1575 m	C=N stretch
1260 m	1220 m	1225 m	1220 m	1220 m	P=O stretch
830 w	850 m	840 m	850 w	855 m	P—O—C
1050 mb	1065 b	1060 b	1060 wb	1065 b	(alkyl)

* Recorded on liquid film, ** recorded on KBr pellets, *** abbreviations used: s, strong; m, medium; w, weak; b, broad.

Table III. Electronic spectra, magnetic moment (300 °K) and molar conductivities (10^{-3} M) of Ni(II) complexes.

Compound	Band position* [cm ⁻¹]		μ_{eff} (B. M.)	λ_{M} [ohm ⁻¹ ·cm ² ·mole ⁻¹]
Ni(DPPG) ₂ (ClO ₄) ₂	**24,815 (7.0)	³ T _{1g} (P) ← ³ A _{2g}	2.45	165**
	14,815 (2.0)	¹ E _g ← ³ A _{2g}		
	13,330 (2.7)	³ T _{1g} (F) ← ³ A _{2g}		
	8,850 (1.7)	³ T _{2g} ← ³ A _{2g}		
Ni(DPPG)SO ₄	**24,815 (4.5)		Diamagnetic	98**
	15,000 (2.5)			
	13,615 (3.1)	. . .		
	10,000 (0.7)			
Ni(DPPG)Cl ₂	**24,815 (3.5)		Diamagnetic	166**
	14,925 (2.3)	. . .		
	13,605 (3.0)			
	9,990 (0.5)			
Ni(DPPG)I ₂	***23,810 (341.5)	¹ A _{1g} → ¹ A _{2g}	Diamagnetic	83***

* Values in parentheses indicate ϵ_{max} , ** in methanol solution, *** in nitromethane solution.

NH stretch of the ligand remains unaltered in complexes, whereas, the NH deformation vibration of the ligand suffers a negative shift of 10–15 cm^{-1} in the complexes. Of more importance is the lowering of the C=N stretching frequency by 15 cm^{-1} , which definitely indicates the involvement of the imino nitrogen atom in bond formation with the metal ion. The P=O stretching frequency, which usually occurs in the range 1350–1250 cm^{-1} , is sensitive to substitution. The presence of OH or NH group in the vicinity of a P=O group generally lowers the P=O stretching frequency by 50–80 cm^{-1} due to hydrogen bonding³³. In DPPG hydrogen bonding possibly occurs. A medium intensity band at 1260 cm^{-1} in DPPG has been assigned to P=O stretching. In the complexes, this band is substantially shifted to lower frequency by ~ 40 cm^{-1} thus manifesting definite interaction of P=O groups with metal ion. As expected the bands due to P–O–C (alkyl) vibrations of the ligand remain unaltered in the complexes. From IR spectra it is apparent that DPPG acts as a tridentate ligand and bonding takes place from two P=O groups and the imino nitrogen atom. In the ionic perchlorate with T_d symmetry, the ν_3 and ν_4 bands, which are IR active, appear in the region (1160–1050 cm^{-1}) and 940 cm^{-1} . Unfortunately the regions of occurrence of these bands are masked by ligand bands. For coordinated sulphate (depending on the nature of coordination) ν_3 and ν_4 bands split, but such regions are also overlapped with ligand bands, thus rendering IR spectra ineffective in deciding the nature of anion participation.

All but the perchlorate complex are diamagnetic (Table III) indicating square planar geometry of

1:1 complexes. The perchlorate complex as expected shows a magnetic moment for two unpaired electrons, confirming the tridentate nature of the ligand. If the 1:1 complexes are accepted to have square planar geometry, evidently sulphate ion acts as an unidentate ligand.

The molar conductance data of the complexes are summarised in Table III. Unfortunately, except for the iodo complex others do not have enough solubility in nitromethane. The conductance value of the iodo complex is compatible with a 1:1 electrolyte. Other DPPG complexes in methanol exhibit 1:2 electrolytic behavior, which indicates that the complexes get extensively solvated.

The electronic spectra of perchlorate complexes indicate typical octahedral environment around the metal ion. The corresponding transitions are noted in Table III. Ni(DPPG)I₂ in nitromethane exhibits a single band at 23,810 cm^{-1} due to $^1A_{1g} \rightarrow ^1A_{2g}$ transition for square planar complexes. In Fig. 1 the spectra of nickel chloride (a), Ni(DPPG)Cl₂ (b) and the latter complex with excess ligand in methanol solution (c) have been compared in the

Figure. Visible spectra of nickel chloride and Ni(DPPG)Cl₂ in methanol.

range 600–850 nm to investigate the solvation phenomenon of Ni–DPPG complexes. While (b) suffers a blue shift with respect to (a), the molar extinctions of (c) increase as against (b) though their band positions remain unchanged. This leads to conclude that during solvation in (b) the ligand does not get detached from the complex and the curve (c) is perhaps due to formation of $[\text{Ni}(\text{DPPG})_2]^{2+}$. Further evidence for reversible solvation behaviour was obtained from the fact that the red iodo complex turns green in methanol and again becomes red on removal of methanol.

It is imperative at this stage to mention that though the amino group has marked affinity for coordinating with nickel ion, in DPPG amino nitrogen atoms are not coordinately bound. Apart from the steric factor, it may be reasonably assumed

that the nitrogen lone pair is involved in $p\pi-d\pi$ bonding³⁴ with the empty d orbitals of the neighbouring phosphorus atom. As coordination through the oxygen atoms would reduce the $p\pi O-d\pi P$ back bonding, the nitrogen lone pair would tend to delocalise more into the empty d orbitals of the adjacent phosphorus atom.

In conclusion we wish to point out that mono complexes were initially prepared with the hope that some of them might impart a penta-coordination behaviour for nickel, however, such expectation was not met with success. Further work is in progress with other metal ions and related type of ligands (l.c.) to explore this possibility.

Thanks are due to Prof. N. K. DUTT, Head of the Department of Inorganic Chemistry, for his kind encouragement and providing laboratory facilities.

- ¹ N. M. KARAYANNIS, C. M. MIKULSKI, and L. L. PYTLEWSKI, *Inorg. Chim. Acta Rev.* **5**, 69 [1971].
- ² M. W. G. DE BOLSTER, Thesis, Leiden 1972, and references cited therein.
- ³ B. E. BRIDGLAND and W. R. MCGREGOR, *J. inorg. nuclear Chem.* **32**, 1729 [1970].
- ⁴ N. M. KARAYANNIS, C. M. MIKULSKI, L. L. PYTLEWSKI, and M. M. LABES, *Inorg. Chem.* **9**, 582 [1970].
- ⁵ S. H. HUNTER, R. S. NYHOLM, and G. A. RODLEY, *Inorg. Chim. Acta* **3**, 631 [1969].
- ⁶ D. M. L. GOODGAME, M. GOODGAME, and P. J. HAYWARD, *J. chem. Soc. [London]* **1970**, 1352.
- ⁷ E. BANNISTER and F. A. COTTON, *J. chem. Soc. [London]* **1970**, 1873, 1878, 2276.
- ⁸ N. M. KARAYANNIS, C. M. MIKULSKI, M. J. STROCKO, L. L. PYTLEWSKI, and M. M. LABES, *J. inorg. nuclear Chem.* **33**, 2691 [1971].
- ⁹ A. M. BRODIE, J. E. DOUGLAS, and C. J. WILKINS, *J. chem. Soc. [London]* **1969**, 1931.
- ¹⁰ D. BROWN, J. HILL, and C. E. F. RICKARD, *J. chem. Soc. [London]* **1970**, 476, 497.
- ¹¹ J. T. DONOGHUE and R. S. DRAGO, *Inorg. Chem.* **2**, 572, 1158 [1963].
- ¹² J. T. DONOGHUE, E. FERNANDEZ, and D. A. PETERS, *Inorg. Chem.* **8**, 1191 [1969].
- ¹³ M. W. G. BOLSTER and W. L. GROENEVELD, *Z. Naturforsch.* **27b**, 759 [1972].
- ¹⁴ M. W. G. BOLSTER and W. L. GROENEVELD, *Recueil Trav. Chim.* **90**, 477, 687 [1971]; **91**, 171, 477, 643 [1971].
- ¹⁵ J. PHILIP, M. A. MULLINS, and C. CURRAN, *Inorg. Chem.* **7**, 1895 [1968].
- ¹⁶ M. SCHAFER and C. CURRAN, *Inorg. Chem.* **4**, 623 [1965].
- ¹⁷ S. S. ZUMDAHL and R. S. DRAGO, *Inorg. Chem.* **7**, 2162 [1968].
- ¹⁸ N. M. KARAYANNIS, C. OWENS, L. L. PYTLEWSKI, and M. M. LABES, *J. inorg. nuclear Chem.* **31**, 2059, 2767 [1969].
- ¹⁹ N. M. KARAYANNIS, E. E. BRADSHAW, L. L. PYTLEWSKI, and M. M. LABES, *J. inorg. nuclear Chem.* **32**, 1079 [1970].
- ²⁰ N. M. KARAYANNIS, C. M. MIKULSKI, M. J. STROCKO, L. L. PYTLEWSKI, and M. M. LABES, *Inorg. Chim. Acta* **4**, 557 [1970].
- ²¹ D. D. SCHMIDT and J. T. YOKE, *Inorg. Chem.* **9**, 1176 [1970].
- ²² D. F. PEPPARD, *Advances in Inorganic Chemistry and Radiochemistry* **9**, 1 [1966].
- ²³ R. M. DIAMOND and D. G. TUCK, *Progr. in Inorg. Chem.* **2**, 109 [1960].
- ²⁴ T. H. SIDDALL, III, *J. inorg. nuclear Chem.* **25**, 883 [1963].
- ²⁵ T. V. HEALY and J. KENNEDY, *ibid.* **10**, 128 [1959].
- ²⁶ J. A. WALMSLEY and S. Y. TYREE, *Inorg. Chem.* **2**, 312 [1963].
- ²⁷ T. H. SIDDALL and C. A. PROHASKA, *Inorg. Chem.* **4**, 783 [1965].
- ²⁸ C. M. MIKULSKI, N. M. KARAYANNIS, L. L. PYTLEWSKI, R. O. HUTCHINS, and B. E. MARYANOFF, *J. inorg. nuclear Chem.* **35**, 4011 [1973].
- ²⁹ E. UHLIG and M. SCHAFER, *J. inorg. nuclear Chem.* **30**, 3109 [1968].
- ³⁰ A. N. SPECA, L. L. PYTLEWSKI, and N. M. KARAYANNIS, *ibid.* **34**, 3671 [1972].
- ³¹ G. J. SUTTON, *Aust. J. Chem.* **16**, 1134 [1963].
- ³² F. G. SHERIF, *J. inorg. nuclear Chem.* **30**, 1707 [1968].
- ³³ C. N. R. RAO, *Chemical Applications of Infrared Spectroscopy*, A. P. [1963].
- ³⁴ W. E. SLINKARD and D. W. MEEK, *Inorg. Chem.* **8**, 1811 [1969].