NICKEL(II) COMPLEXES OF METHYLPHOSPHINEDIACETIC ACID

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Abstract—Methylphosphinediacetic acid (H₂G) is coordinated to nickel(II) in two different ways, depending on whether its carboxyl groups are protonated or dissociated. The acid behaves as a monodentate tertiary phosphine in that it yields a series of *trans*-square planar NiX₂(H₂G)₂ complexes (X = Cl, Br, NCS or CN) which are stable in the solid state and as solutions in polar non-aqueous solvents. In neutral aqueous solution the NiG₂²⁻ complex is the predominant species (log β_2 = 8.24 at 25°C and I = 0.1) even in excess nickel(II). Solid NiG·4H₂O is the nickel salt of this anion, Ni[NiG₂]·8H₂O. The X-ray structural determination of the barium salt, BaNiG₂·NaClO₄·5H₂O, revealed the uncommon *cis*square planar arrangement around nickel with the G²⁻ anions acting as chelating P,Obidentate to nickel and as O-monodentate to barium. Sodium and perchlorate ions are located between the complex units and, surprisingly, cannot be removed on recrystallization.

Phosphineacetic acids belong to the class of functionalized phosphines which are capable of coordinating metal ions through the soft or hard donor or through both donors simultaneously as chelating or bridging ligands. Depending on the metal ion type and the structure of the particular phosphineacetate, all these coordination modes have been demonstrated for complexes studied in this laboratory.¹ From the ligands investigated, those with the general formula $RP(CH_2CO_2H)_2$ represent a series which offers a possibility of studying the influence of the R substituent on the coordination properties of the potentially terdentate $-P(CH_2CO_2)^{2-}$ group. As expected, the coordination behaviour has been shown to change drastically from $R = C_6 H_5^2$ to $R = C_2 H_5^3$. Hence, a program was developed to synthesize and study several ligands containing R groups with very different steric and/or electronic parameters. The present paper describes nickel(II) complexes of methylphosphinediacetic acid⁴ (H_2G) as the ligand involving the sterically undemanding methyl substituent with a marked +I effect.

EXPERIMENTAL

The synthesis of the ligand⁴ and most of the experimental techniques³⁻⁵ have been described. All manipulations with solutions were carried out in a dry argon atmosphere; the solids are air-stable.

Preparation of the complexes

NiCl₂(H₂G)₂: 1 mmol NiCl₂· 6H₂O and 2 mmol H₂G·HCl were dissolved in a small amount of water and repeatedly evaporated *in vacuo* to dryness with excess acetic acid-benzene (1:1 vol.) until a red crystalline material separated. This was dissolved in hot acetic acid, filtered and allowed to cool slowly. Recrystallization from acetic acid and drying at 80° C/0.2 kPa gave the product in 55% yield.

NiX₂(H₂G)₂ (X = Br, NCS or CN) were obtained by metathesis of the chlorocomplex with stoichiometric amounts of KX in acetic acid, filtration of KCl and crystallization (for X = CN, crystallization was induced by addition of benzene). Yields of the recrystallized (acetic acid) and dried complexes varied between 40 and 70%. The iodo complex could not be obtained pure because of irreversible precipitation of anhydrous NiI₂. For measurements in solution, the complex was freshly prepared by metathesis and removal of KCl by filtration where necessary.

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NiG \cdot 4H₂O: 1 mmol H₂G \cdot HCl was dissolved in 4 cm³ water, neutralized by 1.5 mmol Li₂CO₃ and mixed with 1.02 mmol hydrated nickel(II) perchlorate. The product was precipitated by slow addition of excess ethanol. After washing with ethanol and drying at 25°/0.2 kPa the yield was 85%.

BaNiG₂ · NaClO₄ · 5H₂O : 4.00 mmol H₂G · HCl, 2.00 mmol hydrated nickel(II) perchlorate and 2.00 mmol hydrated barium(II) perchlorate were dissolved in 6.00 cm³ 2.00 M NaOH. After addition of 6 cm³ ethanol at 60°C and cooling, the product suddenly crystallized out. It was recrystallized twice from 50% (vol.) aqueous ethanol and dried at 25° C/0.2 kPa with an overall yield of 65%.

CAUTION: the compound detonates violently on heating above 230°C.

Numerous attempts to obtain a product of this type in the absence of sodium and/or perchlorate ions failed.

The samples containing ⁶⁴Ni were prepared from ⁶⁴NiO (Tekhsnabeksport, U.S.S.R.) by scaling down the procedures outlined.

Analytical data for all the new compounds (C, H, Ni, P, halogens, N, Na, Ba and H₂O where appropriate) agreed with the calculated values within ± 0.5 relative %.

Crystal structure determination

The preparation of single crystals of $BaNiG_2$. $NaClO_4 \cdot 5H_2O$ involved considerable difficulty, mainly because of the notorious tendency of needlelike crystals to aggregate along the needle axis. Finally, 0.2 mmol NiBr₂(H_2G)₂ dissolved in 1 cm³ water was neutralized with 0.4 cm³ 2 M NaOH, and the solution was poured into a long 5-mm internal diameter test tube and mixed with 1.4 cm³ of a freshly prepared 5% gelatine solution in 50 vol. % aqueous ethanol. After formation of the gel, a solution of 0.2 mmol Ba(ClO₄)₂·3H₂O in 2 cm³ ethanol was carefully layered on the top, the tube was sealed and left undisturbed for 2 weeks at room temperature. Crystals which formed in the gel layer were isolated by thorough decantation with 70 vol. % and then absolute ethanol. Their identity and quality was confirmed by Weissenberg photographs. The sample chosen for X-ray measurement was about $1.0 \times 0.15 \times 0.04$ mm³. 6898 reflections were collected for $3^{\circ} < 2\theta < 54^{\circ}$. 5244 asymmetric data yielded a final number of 4386 strong reflections with $F > 4\sigma$. The symmetry is triclinic, space group $P\overline{1}$, a = 6.991(2), b = 11.470(3), c = 15.341(3) Å, $\alpha = 102.09(2)^{\circ}$, $\beta = 91.60(2)^{\circ}$, $\gamma = 90.47(2)^{\circ}, V = 1202.2(5) \text{ Å}^3, d_m = 1.99 \text{ (flo-}$ tation in bromoform-benzene), $d_x = 2.02 \text{ g cm}^{-3}$,

 $Z = 2, R = 0.045, R_w = 0.040$, and the number of refined parameters is 331. The measurement was carried out on a Nicolet R3m diffractometer. The radiation was $Mo-K_{\alpha}$, the unit cell was refined using 16 reflections, and the Wykoff scan from 2.0 to 29.3° min⁻¹, scan width 1.0° . Structure determination using direct methods (SHELXTL), anisotropic refinement of non-hydrogen atoms, the hydrogen atoms were calculated for ideal tetrahedra and refined in rigid groups. Isotropic hydrogens, water hydrogen atoms with a fixed temperature factor of 0.1. The last refinement used a weighting scheme with $w = 1/\sigma^2[R_w]$. Final atomic coordinates, thermal parameters and a list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The properties of the complexes are summarized in Table 1.

H_2G as the ligand

Analogously to other monophosphineacetic acids, H_2G in non-aqueous solvents of medium polarity coordinates to nickel(II) as a monodentate phosphine forming complexes of the NiX₂(H₂G)₂ type. Their properties in the solid state and in solution are consistent⁶ with the familiar *trans*-square planar structure and with uncoordinated, strongly hydrogen-bonded ligand carboxyl groups. The *trans* geometry follows unambiguously from the number of isotope-substitution-sensitive bands in the far-IR spectra.^{5,7} As is usual for nickel(II) complexes, the thiocyanate is N-bonded.⁸

With the exception of the cyano complex, all members of the series decompose instantaneously in water to yield H₂G and NiX₂. The solutions in non-aqueous solvents contain monomeric molecules of the complexes, are non-conducting, and their UV-VIS spectra are identical with the solidstate spectra. The conductivity of the aqueous solution of $Ni(CN)_2(H_2G)_2$ can be explained by a partial dissociation of carboxyl protons as indicated⁹ by the solution IR spectrum. In contrast, the Ni—CN bond persists even in a strong acid. All the complexes are kinetically labile as indicated by their NMR spectra consisting of broad bands. The spectra become sharper on cooling but remain unresolved at -40° C which is the temperature where the solubility of the samples becomes impractically low. Hence, the only information from the NMR spectra is the coordination shifts which exhibit usual trends suggesting a strong $P \rightarrow Ni\sigma$ interaction.

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Compound	Colour [m.p. (°C)]	$\mathrm{UV-VIS}^{d}$ $\tilde{\mathrm{v}}_{\mathrm{max}} \left(10^{-3} \mathrm{cm}^{-1} \right) \left(\varepsilon_{M} \right)$	IR^{b} $\tilde{\mathrm{v}}_{\mathrm{max}} (\mathrm{cm}^{-1})$	NMR [¢] ð (ppm)	Remarks
NiCl ₂ (H ₂ G) ₂	Red [152 (dec)]	17.1sh, 18.6 (115), 20.9 (320), 28.1 (8900), 34.8sh, 37.3sh, 41.0 (15,600)	3170vs, 1693vs, 1292s COOH 407m [11] v(Ni—CI) 260w [14] v(Ni—P)	¹ H : 1.70, 3.22, 9.20 ³¹ P : 6.2	e.
NiBr ₂ (H ₂ G) ₂	Purple [150 (dec)]	15.1sh, 17.5 (970), 20.7 (440), 26.0 (6530), 32.2sh, 36.4sh, 40.3 (23,700)	3170sb, 1693vs, 1293s COOH 383m [11] v(Ni—Br) 259w [16] v(Ni—P)	¹ H: 1.67, 2.62, 10.60 ³¹ P: 5.1	a
Nil ₂ (H ₂ G) ₂ [¢]	Olive green	16.5 (270), 22.2 (1890), 26.6 (3520), 31.5 (3890), 35.4 (11,600), 39.4 (5820)		'H :⁄ 1.76, 2.58, 10.71 ³¹ P :⁄ 4.7	Ø
Ni(NCS) ₂ (H ₂ G) ₂	Orange [159–161 (dec)]	19.5sh, 20.9sh, 27.3 (1470) 35.0 (4710), 37.3sh, 42.2 (5950)	3170sb, 1714vs, 1290s COOH 2090vs v(C=N), 445w δ(NCS) 418m [11] v(Ni-N) 256w [8] v(Ni-P)	'H: 1.69, 3.11, 10.72 ³¹ P: 8.3	۵
Ni(CN) ₂ (H ₂ G) ₂	Yellow [210–230 (dec)]	22.2sh, 24.3 (1400), 33.7sh, 36.6sh, 40.5 (18,600)	3170sb, 1712vs, 1299s COOH 1710vs, 1588m COOH + COO ^A 2110m v(C≡N) 255vw [9] v(Ni—P)	¹ H: 1.73, 3.21m 10.80 2.05, 3.53 ⁴ ³¹ P: 11.8, 14.2 ⁶	51
NiG • 4H ₂ O	Greenish yellow [260-270 (dec)]	9.8 (5), 16.2 (8), 24.5 (200), 26.2sh, 37.0 (2210), 41.5 (6800)	3360vs, 3275s, 1640m H ₂ O 1600vs, 1370vs COO 249w [6] v(Ni—P)		-
BaNiG2 • NaClO4 • 5H2O	Golden yellow [/]	24.6 (365). 37.6 (4400), 42.0 (13,900)	3420vs, 1635sh H ₂ O 1610vs, 1380s COO 1144m, 1086s, 912m, 624w ClO 251w [8] v(Ni—P) 1588vs, 1630sh COO ⁴	¹ H. ⁴ 1.98, 3.72 ³¹ P. ⁴ 23.0	×
^a Band positions in THF solut ^b Only bands of diagnostic val ^c In d_8 -THF unless stated othe ^d Diamagnetic; non-conductin ^e Solution properties in acetic. ⁷ In CD ₃ CO ₂ D.	ions (except where stated of ue are given; bands sensitiv srwise; all bands are broad; ug in solution. acid.	therwise). /e to isotopic substitution with ữ(Ni)–ỹ singlets.	${}^{\theta}_{L}$ ${}^{\mu}_{L}$ ${}^{\mu}_{L}$ ${}^{\mu}_{D}$	iamagnetic; $\Lambda_M = 82 (H_2O, ried samples in D_2O solution \pi = 2.9 BM per two formula ecomposes explosively at 235° biamagnetic; \Lambda_M = 190 (H_2O)$	0.01 M). units. C. . 0.01 M).

Nickel(II) complexes of methylphosphinediacetic acid

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G^{2-} as the ligand

In aqueous solution, the G^{2-} anion coordinates to nickel(II) with the formation of the NiG₂²⁻ complex anion. The Ni(ClO₄)₂- G^{2-} -H⁺ system was studied potentiometrically with a glass electrode at 25°C, I = 0.1(Na)ClO₄, total G = 0.002 and 0.003 M, 0.0004 < total Ni < 0.006 M, 1.8 < log H⁺ < 12.5, and the stability constants obtained by the standard data treatment¹⁰ are :

$$\begin{split} &\log \beta_{120} = \log [\text{NiG}_2] / ([\text{Ni}][\text{G}]^2) = 8.24(6), \\ &\log \beta_{121} = \log [\text{NiHG}_2] / ([\text{Ni}][\text{H}][\text{G}]^2) = 12.5(2), \\ &\log \beta_{122} = \log [\text{NiH}_2\text{G}_2] / ([\text{Ni}][\text{H}]^2[\text{G}]^2) = 16.1(2) \end{split}$$

(charges omitted). Interestingly, no detectable amounts of 1:1 complexes are formed in the system under the given experimental conditions.

The properties of the complexes containing the NiG_2^{2-} anion suggest a square-planar arrangement involving the ligand as bidentate P.O-chelating with one carboxylate group free and thus easily protonated. Further protonation destroys the NiG₂ core completely. The formally 1:1 solid compound, NiG·4H₂O, should be certainly formulated as $Ni[NiG_2] \cdot 8H_2O$: the nickel(II) ion outside the NiG₂ core seems to be coordinated by water molecules and/or intra- and intermolecular carboxyl oxygens in a pseudo-octahedral arrangement, analogous to dinickel(II) ethylenediphosphinetetraacetate.^{1(e),5} The structure of the barium salt of the complex anion represents a problem of special interest. Firstly, the compound contains the stoichiometric amount of sodium perchlorate which cannot be removed on recrystallization from aqueous ethanol. The IR spectrum indicates that

the perchlorate is present as the ionic species. Secondly, the geometry of the (presumably planar) nickel coordination environment remains unclear on the basis of the spectral data: down to the temperature where measurements in aqueous methanol are possible, the complex is NMR-labile and the spectra thus yield no information about the P-CH₂ virtual coupling;¹¹ further, the IR spectrum is obscured by ligand bands in the region where the isotopic shifts of v(Ni-O) should be of diagnostic value. However, the solution IR spectrum clearly shows the presence of two types of COO groups.⁹ Consequently, an X-ray structural determination was undertaken.

The perspective view of the structure together with the atom numbering is depicted in Fig. 1 and the stereoview of the unit cell in Fig. 2. Table 2 summarizes the important distances and angles. The structure consists of NiG_2^{2-} complex anions with P,O-chelating ligands; the uncoordinated carboxyls form ionic bonds to barium(II). Hence, the G^{2-} anion should be formally considered as a simultaneously chelating and bridging terdentate ligand, which is a novel bonding type among phosphineacetates. The interspace available permits almost exact accommodation of perchlorate and sodium ions, thus probably explaining why analogous compounds without sodium perchlorate could not be prepared.

The conformation of the chelate rings and, consequently, the pertinent bonding distances and angles differ from one ring to another but are all unexceptional. As usual,¹ the main distortion of the ligand resulting from its coordination is located on the phosphorus atom with bonding angles varying between 97.4 and 125.8°. For the carboxylate



Fig. 1. Perspective view of the structure of $BaNiG_2 \cdot NaClO_4 \cdot 5H_2O$ with closest intermolecular contacts. Hydrogen atoms (omitted for clarity) are given the numbers of their bonding partners. W denotes the oxygen atom of a water molecule. For symmetry code, see Table 2.

	(a) N	li environment	
Ni—P(1)	2.139(2)	P(1)NiP(2)	100.8(1)
Ni-P(2)	2.137(1)	P(1)—Ni—O(12)	85.9(1)
NiO(12)	1.903(3)	P(1)—Ni—O(22)	173.1(1)
NiO(22)	1.907(4)	P(2)—Ni—O(12)	172.8(1)
		P(2)—Ni—O(22)	86.1(1)
		O(12)—Ni—O(22)	87.2(2)
	(b) B	a environment	
Ba—O(14)	2.695(5)	BaO(13) ⁱⁱⁱ	2.805(5)
Ba—O(23)	2.687(5)	$Ba - O(14)^{iii}$	2.888(5)
BaW(1)	2.861(4)	Ba—O(12) ^v	2.905(4)
$Ba - W(1)^{iv}$	2.901(4)	Ba—O(22) ^v	2.853(5)
Ba—W(4)	2.855(7)		
	(c) N	a environment	
Na—W(2)	2.264(12)	W(2)-Na-W(3)	118.5(4)
Na	2.440(8)	W(2)-Na-W(5)	109.6(5)
Na-W(5)	2.320(13)	W(3)NaW(5)	131.8(4)
Na-0(11) ⁱ	2.345(4)	O(11) ⁱ —Na—O(21) ⁱⁱ	168.3(2)
Na-0(21) ⁱⁱ	2.332(4)	O(11) ⁱ —Na—W,	
		O(21) ⁱⁱ —Na—W(mean)	90(5)
	(d) C	ll environment	
Cl—O(31)	1.332(9)	O(31)—C1—O(32)	109.6(7)
Cl—O(32)	1.327(13)	O(31)-C1-O(33)	111.0(6)
Cl-O(33)	1.409(7)	O(31)ClO(34)	109.7(6)
Cl-O(34)	1.420(8)	O(32)—C1—O(33)	110.1(6)
		O(32)ClO(34)	107.2(6)
		O(33)ClO(34)	109.1(5)
	(e) Intern	molecular contacts	
W(1)—Ba ^{iv}	2.901(4)	BaW(1)Ba ^{iv}	110.3(1)
$W(1) - O(11)^{iii}$	2.791(6)	BaW(1)O(11) ⁱⁱⁱ	105.6(2)
W(1)O(23) ^v	2.846(7)	BaW(1)O(23) ^v	122.3(2)
., .,		$Ba^{iv} - W(1) - O(11)^{iii}$	90.8(1)
		$Ba^{iv} - W(1) - O(23)^{v}$	112.8(2)
		O(11) ⁱⁱⁱ —W(1)—O(23) ^v	110.1(2)
W(2)O(24) ^{vi}	2.882(12)	NaW(2)O(24) ^{vi}	138.2(5)
W(3)O(13) ⁱ	2.797(8)	$Na-W(3)-O(13)^{i}$	108.3(2)
W(3)—O(24) ⁱⁱ	2.763(8)	Na-W(3)-O(24) ⁱⁱ	111.6(2)
		$O(13)^{i}$ W(3)O(24) ⁱⁱ	124.5(3)
W(4)O(21) ^v	2.842(8)	BaW(4)O(21) ^v	88.1(2)
W(5)—O(33) ^v	2.786(14)	Na—W(5)—O(33) ^v	173.3(4) ^b

Table 2. Important bond distances (Å) and angles (°) with esds in parentheses^a

^aW denotes the oxygen atom of a water molecule. Symmetry code: i, 1-x, -y, 1-z; ii, 1-x, 1-y, 1-z; iii, 2-x, -y, -z; iv, 3-x, -y, -z; v, x+1, y, z; vi, x, y, z + 1. ^bNot assumed to be hydrogen bonding.



Fig. 2. Stereoview of the unit cell down the a-axis.

groups bonded to nickel, the carbonyl and hydroxyl C—O distances can be safely distinguished (1.218, 1.206, 1.306, 1.317 Å, respectively), suggesting a high degree of covalency of the Ni—O bond. In contrast, the carboxylate bonds to barium are ionic with a mean C—O distance of 1.238(7) Å.

The environments of all three cations are more or less unusual. The nickel(II) coordination polyhedron represents a rare example of the *cis*-square planar monophosphine complex for which, to our knowledge, only one other representative has been safely authenticated.¹² The NiP₂O₂ moiety is planar within ± 0.04 Å and the distortion of the angles from an ideal square is attributable to the bulkiness of phosphorus. The available data suggest that there is a general tendency for P,O-chelating phosphineacetates to assume the P,P-*cis* arrangement in complexes of Group VIII metals,^{1(b),(c),(e)} forming chelate rings of very similar envelope conformations irrespective of the metal ion type.

The environment of barium(II) includes nine oxygen atoms from water molecules and intra- and intermolecular carboxylate groups. As expected, the intramolecular bonding distances to O(14) and O(23) are considerably shorter than the remaining Ba-O contacts; consequently, the geometrical arrangement is distorted and does not seem to be simply related to any of the ideal polyhedrons calculated for the hard-sphere model.¹³ Roughly stated, the BaO₉ moiety can be approximated as a pentagonal bipyramid with doubled axial positions and barium in the centre: the O(14) and O(23)atoms together with three water molecules constitute an approximate equatorial plane (within ± 0.34 Å including barium) yielding, probably by chance, the exact theoretical O-Ba-O angle of 72(6)°. Four intermolecular carboxylate oxygens arranged as two couples, $O(13)^{iii} + O(14)^{iii}$ and $O(12)^v + O(22)^v$, complete the arrangement at the two doubled axial positions. The straight line connecting the centers of gravity of the two couples of oxygen atoms intersects the mean equatorial plane at an acceptable angle of 85.7° and at a distance of only 0.25 Å from barium. The two pairs of axial oxygens adopt a staggered conformation with a dihedral angle of 45.8° between the Ba-O(13)ⁱⁱⁱ-O(14)ⁱⁱⁱ and Ba-O(12)^v-O(22)^v planes.

The environment of sodium(I) is a distorted trigonal bipyramid with three water molecules forming an equatorial plane (within ± 0.03 Å including sodium) and with two intermolecular carboxylate oxygens at the axial positions.

The water molecules are coordinated at barium and sodium; W(1) acts as a bridge between two adjacent barium ions. The hydrogen atoms of the water molecules could not be located precisely but, according to the geometry of O...O contacts,¹⁴ are likely to be involved in hydrogen bonding to carboxylate oxygens (Table 2). The various degrees of participation of the water molecules in coordination and hydrogen bonding conform to the temperature factors of the water oxygen atoms.

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